AT&T

Software for Automated Powder Diffraction

APD3720

Operation Manual

4835.015.14000

2nd Edition 1987

Philips Electronic Instruments, Inc.
85 McKee Drive
Mahwah, NJ 07430

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READER´S COMMENT FORM

If you have any comment on this manual, will you please complete the attached form and return it to :

Product Manager
Analytical X-Ray,
Philips Electronic Instruments, Inc.,
85 McKee Drive
Mahwah NJ 07430

Comment:

Suggested addition or alteration:

Please attach any neccessary additional sheets.

Your name : Firm : Position :

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SOFTWARE PERFORMANCE REPORT

4835.015.14000

If you have any software faults, please complete this form and return it to:

Product Manager
Analytical X-Ray,
Philips Electronic Instruments, Inc.,
85 McKee Drive
Mahwah NJ 07430

Name: _ Date: _ _ _ _ _ _ _ _

Firm: _

Address: _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _

_ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _

Country: _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _

Type number of software package: .....

Microprocessor software.
Description: .....

Version: .....

Minicomputer software.
Description: .....

Version: .....

Computer type	Operating system	Memory size

System device	Distribution Medium	

Report type/priority:

- o Problem/error
- o Suggested enhancement
- o Other
- o Heavy system impact
- o Moderate system impact
- o No significant impact
- o Documentation/Suggestion

Can the problem be reproduced at will? o Yes o No

Peripherals used:

Type	Connected to	Baud rate
1. _ _ _ _ _ _ _ _ _	_ _ _ _ _ _ _	_ _ _ _ _
2. _ _ _ _ _ _ _ _ _	_ _ _ _ _ _ _	_ _ _ _ _
3. _ _ _ _ _ _ _ _ _	_ _ _ _ _ _ _	_ _ _ _ _
4. _ _ _ _ _ _ _ _ _	_ _ _ _ _ _ _	_ _ _ _ _
5. _ _ _ _ _ _ _ _ _	_ _ _ _ _ _ _	_ _ _ _ _
6. _ _ _ _ _ _ _ _ _	_ _ _ _ _ _ _	_ _ _ _ _

Sample changer
Special uP software .....

X-ray/beta/gamma/OE Spectrometer/Diffractometer

Type number: ..... Serial number: .....

Attachments: o Floppy o Listing o Other

Attach the original terminal input and output (hard-copy) to show the error. The output should show the version number of the software in use.

For later versions of minicomputer software, special indirect command procedures are available to give information about the computer system.

Complement with the following data (if applicable):

- Directory of disc
- Contents of the parameter bank
- Contents of system parameters
- Contents of all disc files concerning the problem

Description of the problem:

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PERTAINS TO PHILIPS ELECTRONIC INSTRUMENTS
APD3720 AUTOMATED POWDER DIFFRACTOMETER.

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1.1 INTRODUCTION

The APD1700 Automated Powder Diffractometer system is the most modern available today. It can be used to automate several diffractometers by:

- Collecting data.
- At the same time as it collects data, it can be treating previously collected data.
- Analysing the results of data treatment.
- Printing or plotting the results of analysis.

Up to four PDP or MicroPDP users at a time can perform one or more of these tasks using up to four diffractometers; and yet the APD1700 is still very easy to use, as will be explained in the following chapters.

The Professional 300 series personal computers 350 or 380 (hereafter Professional 350/380) can be used for two diffractometers by one user.

NOTE: The VAX computer is only used for data manipulation and analysis, and will probably already be installed and used for other tasks, therefore, some of the following remarks may not be relevant.

1.2 SHORT DESCRIPTION OF THE SYSTEM

The APD1700 system consists of one or more x-ray powder diffractometers, a mini computer with peripherals, and the APD1700 software system.

The main components of a diffractometer are: an x-ray generator, a goniometer with stepping motor and detector, a radiation shield, and PW1710 diffractometer control and interface. Other devices such as: automatic divergence slit, graphite monochromator, and automatic sample changer may be included, and in many instances are necessary extensions.

A DEC* VAX computer with VMS, a PDP-11 computer with RSX-11M, a MICRO/PDP-11 microcomputer with Micro/RSX or RSX-11M, or a Professional 350/380 with P/OS operating system is a necessary pre-requisite for the software programs. The interactive nature of the operating system is fully exploited in the APD software.

* DEC, VAX, VMS, PDP, RSX, Professional, P/OS and VT are trade marks of Digital Equipment Corporation.

A large variety of peripheral equipment can be connected to the PDP-11 computer:

- Normally two disk drive units are built in, a magnetic tape unit can also be part of the system.
- A system printer and/or a plotter can be arranged so that several users can have data or results printed or plotted on them.
- Operator terminals can be used to give commands to, or receive messages from the APD system. These terminals can be graphics terminals, alphanumeric video terminals and/or printing terminals.

NOTE: Up to four operator terminals can be used at the same time to run APD programs.

The same variety of peripheral equipment is available for the MicroPDP-11 computer, in which normally one Winchester disk and two floppy disk drive units are built in.

The Professional 350/380 computer has one Winchester disk drive and two floppy disk drives built in, it is equipped with one operator terminal and can be extended with a system printer.

The VAX computer can be used with the same operator terminals, plotter and printer as the PDP-11.

The APD1700 software package provides the possibility of highly interactive use, for example: the visual comparison and evaluation of data and results. Alternatively, it can perform unattended automatic analyses, for example: data collection, data treatment, and analysis of up to 21 or 42 samples in a sample changer can be performed. These jobs can even be done overnight or on weekends. It is possible for the system to perform unattended automatic analyses at the same time as you are using it interactively.

Figures 1.1 and 1.2 show the maximum configurations of APD1700 with PDP-11, MicroPDP-11 and Professional 350/380 systems. Extended memory capacity is necessary in such large configurations.

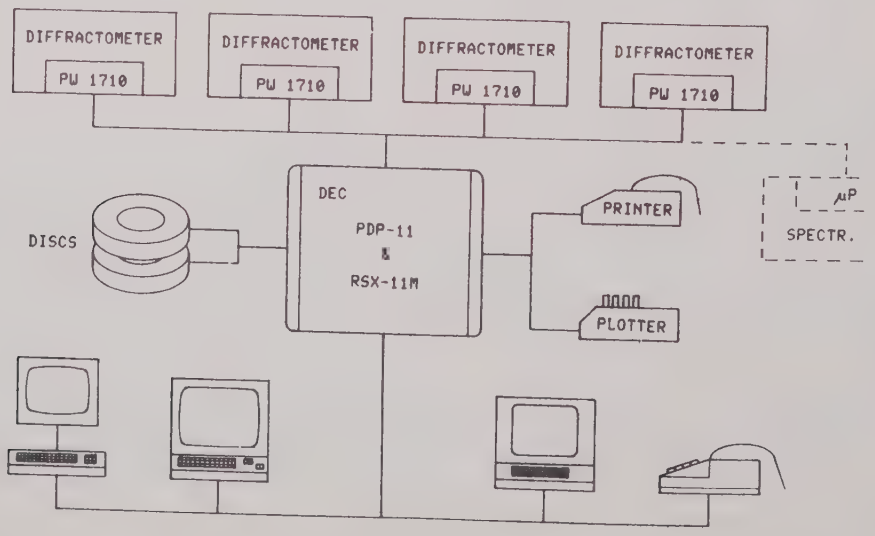

Figure 1.1 Block Diagram of PW1700 Hardware Configuration (PDP and MicroPDP)

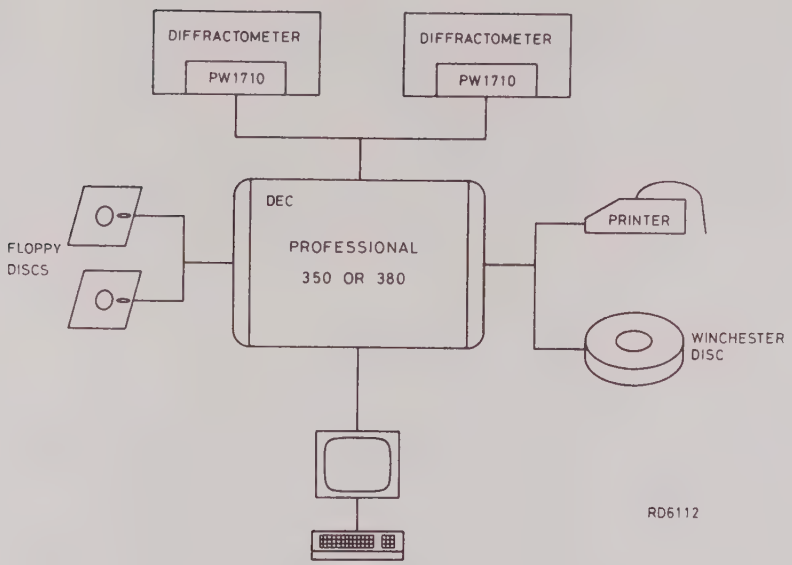

Figure 1.2 Block Diagram of PW1700 Hardware Configuration (Professional 350/380)

The software package is made up according to particular requirements from a large selection of programs together with the APD1700 main program. These programs are shown schematically in Figure 1.3, they are:

* The SYSTEM PREPARATION program. Before any data collection, data treatment, or analysis can be done, the system has to be prepared: by means of manual (keyboard) input of measurement and calculation parameters, by correction of goniometer angles for systematic errors, by editing reference data bases for phase identification, and by determination of calibration constants for quantitative analysis.

  - The REFERENCE DATA BASE program is an optional extension (PW1862) to the APD kernel package (PW1867).
  - The CALIBRATION program is part of the QUANTITATIVE ANALYSIS option (PW1863).

* The DATA COLLECTION program (PW1866). This program enables the execution of data collection on either a single sample, or a batch of samples, with the option of measuring a priority sample or to interpose the measurement of a sample. It enables a report to be made on the status of ongoing experiments. Also the data collected so far in an ongoing experiment can be displayed (printed on a non-graphics terminal and plotted on a graphics terminal). Finally it can be used to halt experiments on one or more diffractometers.

* The PATTERN TREATMENT program. With this program it is possible to treat diffraction patterns, or raw data, or even intermediate results, with different processes before further evaluation or final analysis is made.

  Possibilities that exist, are for example: to do a peak search for crystalline diffraction lines or maxima of "amorphous" materials, to correct systematic diffractometer errors, to eliminate the K-alpha$_2$ component from the raw data file, or to smooth the data. A further possibility with this program is that you can input or edit a DI file (see abbreviations paragraph 1.4) via a keyboard.

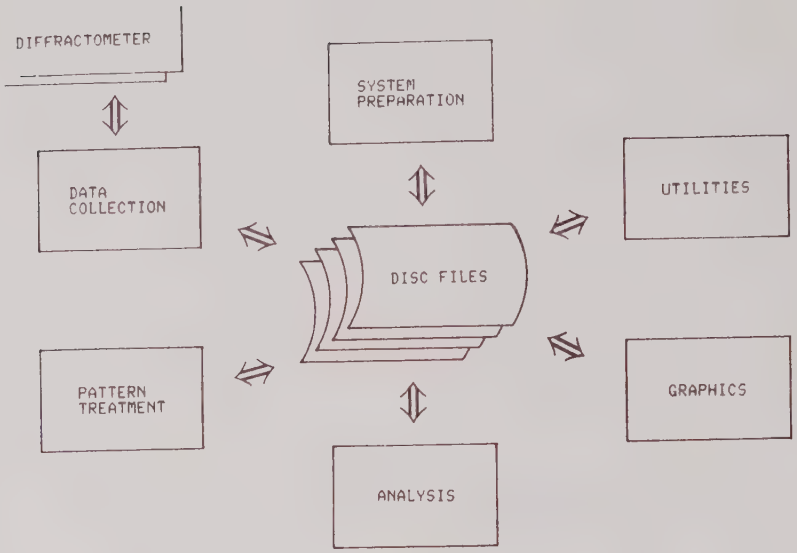

Figure 1.3 Block diagram of APD1700 Software

* The GRAPHICS program. This program enables measurement results (RD files) and/or intermediate results (DI files, and so on) to be drawn on a graphics terminal or a digital plotter for visual evaluation/interpretation. It is also possible with this program to compare raw data files or DI files with reference patterns. DI files and/or reference patterns can be subtracted from or added to each other.

  When using this program, a graphics cursor can be used as an aid during evaluation, or to highlight certain features and enter text to the plot.

* The ANALYSIS program. Up to five (optional) programs can be used to analyse data that has been collected. These programs are:

  - Phase identification (search-match PW1861)
  - Quantitative analysis (PW1863)
  - Line profile analysis (PW1864)
  - Crystallographic analysis (PW1865)
  - Stress analysis (PW1868)

  The results of one type of analysis program may well be used as an aid in another analysis program.

* The UTILITIES program. Utilities are a set of auxiliary programs for various purposes:

  - Disk file handling
  - A facility to perform diffractometry related calculations
  - The possibility to use the PW1710 microprocessor directly.

* The LIST program. This program can provide a listing on your terminal (or the system printer) of each parameter file that has been assembled, and/or a listing of each data file. On the terminal it is possible to partially display parameter files (for example: Terminal system parameters), but on the system printer they are always printed in full. Data files can be printed/displayed partially or in full, the restrictions to this are described in the data treatment/analysis chapters.

* The EXIT command. When you give this command the system leaves the APD main menu (not when a measurement is in progress) so that you can use other programs, or the operating system´s facilities, or you can logout or shutdown the system.

* The HELP program. Information is available for each menu, and at many places during dialogue. The text will be displayed when you type "?".

1.3 HOW TO USE THIS MANUAL

The APD1700 Automated Powder Diffractometer system is easy to use and this manual is meant to inform you how to make the best use of your system. The first few chapters describe the system, give general information, and explain how to start the system. From Chapter 7 onwards the information provided is related to specific programs in the software, and the chapter titles are the same as for those programs. The sub-headings within the chapters have the same names as the sub-programs in the programs, and are in the same sequence as they appear in the programs. There are five Appendices at the end of the book, they show five actual "worked" examples: Phase identification, Line profile analysis, Crystallography, Stress and Quantitative analysis. Finally, at the end of the manual is an alphabetical INDEX of terms and words used in the manual.

The system should be installed in accordance with the Equipment Installation Manuals and the Software Instruction Manual.

Before installing and using APD1700 you should read the Software Instruction Manual. This manual provides information about the installation and operation of the PW1211 Operating System, some information about the terminal settings, and information about the installation of APD1700. If the APD1700 is to be connected to a large computer system that also performs other tasks, you should discuss the installation and start-up with the system manager.

In the chapters dealing with the different program modules, simple examples are provided. If you are a first-time user, we advise you to work through those examples in order to get used to the system.

In examples of actual dialogue, the operator input is either shaded or underlined. The input and output of dialogue will be described between quotes ("INPUT") in this manual. Text that would normally be placed between double quotes is printed between single quotes from here on (for instance: ´worked´ examples).

In the software you can call for help text to be displayed in situations where choices have to be made. Most help text refers to the chapter of this manual where you can find more detailed information on the subject. In this way the manual can be very conveniently used as a reference book, even for the more experienced user.

1.4 ABBREVIATIONS USED IN THIS MANUAL

2D	Second Derivative file
A2	Results of K-alpha$_2$ stripping (data file)
AMORPH	Command - Locate "AMORPHOUS" peaks
APD	Automated Powder Diffraction
APR	April
AUG	August
BK	Background file
<CR>	(Carriage) Return
CRT	Video terminal (Cathode Ray Tube)
D1 - D9	Results from Subtract (data file)
D01 - D99	Parameter files
DAT	Parameter file
DCL	Digital Command Language
dD/D	Delta d over d (d-spacing)
DEC	December
DEC*	Digital Equipment Corporation*
DEF	Default
DEL	Delete (a) file(s)
dev	device
DI	d-spacings and Intensities file
DIR	(display) Directory of files
DMP	Dump file contained in a queue for system printer or plotter
E	Exit (from the APD program = return to the operating system)
EC	Systematic Error Correction file
EqDE	Equivalent Displacement Error of the sample in micro-metres. Calculated from the average deviation of the measured peak position from the reference peak position
FC	Fourier Coefficients file
FCS	File Control Services
FEB	February
FEP	Frequently Encountered Phases (a subfile of the powder diffraction data base)
G	Go
g	group of users in UFD
HEL	Hello (to the system): Log in
HP	Hewlett Packard
I%	Intensity factor indicating percentage of scaling used
INP	Input command list, file containing commands to be processed by an Automatic Analysis Procedure
JAN	January
JB	Batch file
JCPDS	International centre for diffraction data (formerly the Joint Committee on Powder Diffraction Standards)
JUL	July
JUN	June
LIS	ASCII file of parameters of data listing
LO	LOG out
LOG	LOG (in or out)
m	member of UFD
MAR	March
MAY	May
MCR	Monitor Console Routine
MS	Match Score table/file, result of phase identification (IDENTIFY)

N	No
NBS	National Bureau of Standards (USA) high-quality reference patterns
NOV	November
OCT	October
PDF	Powder Diffraction File
PDP*	Programmable Data Processor
PK	Peak file, data file from which the background is removed
P/OS*	Professional computer operating system
Q	Quit
QI	Quantitative Intensities file
QM	Quality Data Mark (in a match score table) as found on the PDF cards
QP	Quantitative intensities file for `clean` sample Plate.
RD	Raw Data file, result of data collection
RSX*	Resource Sharing Executive (a DEC Operating system for PDP-11 computers)
SANDMAN	Search AND MAtch on Nova (name for phase identification program)
SEP	September
SF	Sub file, for Restrictions in Identify (SANDMAN)
SM	Smoothed data file
SPR	Software Performance Report
UFD	User File Directory
UIC	User Identification Code
VAX*	Virtual Address Executer
VDU	Video terminal (Video Display Unit)
VMS*	Virtual memory system
VT*	Video Terminal (VT100, VT125 and so on, DEC trademarks)
WK	(temporary) Work file, used during data collection
Y	Yes

* DEC, MICRO/PDP, Micro/RSX, Professional, PDP, P/OS, RSX, VAX, VMS, and VT are trade marks of Digital Equipment Corporation.

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2.1 INTRODUCTION

All results of data collection, data treatment, and analysis are permanently stored on magnetic disk as data files. All lists of parameters for measurement or analysis also are stored as disk files.

The data collected from each individual sample is stored and can be retrieved for further evaluation by the data file name.

The data file name consists of (up to) nine alpha-numeric characters, followed by the file type extension of up to three characters, indicating the type of data in the file. The full file specifier (described in the Software Instruction Manual, Chapter 4) contains much more information.

For the name of the raw data file, the system proposes (by default) the first six alpha-numeric characters of the sample identification. If a batch is used for data collection the default file name may also contain the job number, and sometimes the position number of the sample in the changer (refer to Chapter 7.2.2.1.).

Values and commands that are proposed by the system are called DEFAULT values or commands. Defaults will always be the logical choice. You can accept a default, or you can choose another value or command.

Every data treatment sub-program has a default file type for input, and for output. For a raw data file (result of a data collection scan) the type extension is always "RD". In general, your file names should also be logical and easy to remember and understand.

Example: A sample receives the identification: "TEST - SAMPLE". The system proposes the default name: "TESTSA", so data collection stores the results in: "TESTSA.RD".

The latter is the default input file type for the peak search sub-program which has as output: "TESTSA.DI", a list of d-values and relative intensities. This in its turn can be used as input file for several analysis programs.

For more information on disk files and on the operating system, please refer to the: Software Instruction Manual.

2.2 RESERVED FILE NAMES

A number of file names and/or type extensions are reserved (for use by the system) per diffractometer, per user, and per APD system.

2.2.1 Per diffractometer, per user (UFD)

APDANA.DAT contains the Analysis programs for diffractometer system number 1.

APDANA.D01 contains for all Quantitative Analysis programs the analytical and internal standard Phase numbers, and per Phase the background correction and the over-lapping Phase numbers with their over-lap factors.

APDANA.D02 contains Calibration data per calibration standard sample:
- sample identification
- mass absorption coefficient
- total concentration of analytes

APDANA.D03 contains Calibration data per Phase (per standard sample):
- concentration
- intensity (corrected for background and line overlap)
- date of data collection.

APDANA.D10 contains the Peak search parameters for all automatic Identification analysis programs.

APDANA.D11 contains the Search-match (SANDMAN) parameters for all automatic Identification analysis programs

APDPHA.DAT contains the Phases for diffractometer number 1

APDSCN.DAT contains the Goniometer Scans for diffractometer 1

NOTE 1: The file names above indicate that they contain data for diffractometer system number 1. For diffractometers number 2 to 4 the file names are followed by 2 to 4.

For example: APDANA2.DAT, APDANA3.D02, APDPHA4.DAT, APDSCN3.DAT

NOTE 2: Do not delete any of the above-mentioned disk files. You may copy these file types from another user (UFD) and/or another diffractometer. You may delete individual Analysis programs, Phases, or Scans using the Assemble program.

2.2.2 Per User (UFD)

DEFAULTS.APD contains the (latest) options chosen by the user, which will be displayed as defaults in a future dialogue. It contains (amongst other data):
- Latest file name
- Peak search parameters
- Plot defaults
- Calibration defaults
- Quantitative analysis defaults

RESTRICT.SF the Restrictions subfile assembled in Identify

CHEMISTRY.SF contains the Chemistry (elements present) data defined in Identify

2.2.3 Temporary files per UFD

APD1700.DMP print instructions to list a data file at the system printer

APDPLOT.DMP plot instructions to plot files at the plotter

DxANA.INP for the sample which is being handled by the Automatic Analysis Procedure program (x is the number of the diffractometer for which the analysis program was designed)

.WK the work file contains data collection instructions (measurement parameters) for one or more samples, the file name is the name of the batch file, or -if no batch file is used- the raw data file name.

One other temporary file is the DATA COLLECTION log file, printed after data collection, the name is the work file name, extension ".DMP".

NOTE: These files are deleted by the system after the tasks have been completed. If, because of problems, tasks are not completed and such a file is not automatically deleted, then you should delete them yourself in order to keep space on the disk and avoid unnecessary warnings.

2.2.4 Per APD1700 System

APDSYS.DAT contains the System parameters

APDTABLES.DAT contains tables of wavelengths and mass absorption coefficients for various tube anode materials

INTTABV2.COD contains translation tables for the coding of crystal structures

IDEANA.INP contains the ´master´ input text file for the automatic identification procedure, from which DxANA.INP files are made

QUAANA.INP contains the ´master´ input text file for the automatic quantitative analysis procedure, from which DxANA.INP files are made

NOTE: These disk files (contained in UFD [1,2]) must never be deleted!

2.3 FILE MANAGEMENT

Almost all actions of the system start out or end up as a file. Although all routine file handling is performed automatically by the program, a few file manipulations have to be initiated by yourself for your file management. You do not need to know where files are physically located on the disk, the system takes care of that.

Therefore in the Utilities program the File handling option is provided within the APD software. The commands in the Utilities program are a subset of the operating system commands. All commands are available to you if you Exit from APD (if the $ prompt is visible). When using a Professional 350/380 system the main P/OS menu appears after exit from APD.

With the small set of tools provided by the APD File handling option, you can:

- Sort the files in a directory into alphabetic order. A directory is more surveyable after sorting.
- Copy a file from one disk (or UFD) to another, (not possible with Professional 350/380 version of APD1700).

  In this way ´old´ raw data files can be stored on a disk, that is put into an archive, and then those files can be deleted from the system disk, thus providing more space for further data. This is described in the Software Instruction Manual Chapter 6.

Copying of a complete disk for back-up purposes is done with the special "BACKUP" program, refer to the Software Instruction Manual Chapter 6. In the "BACKUP" program the disk files are arranged contiguously.

- Delete a file which is no longer useful. With the delete command ´wild cards´ are not accepted, a file must be specifically defined to avoid inadvertent deletions.

  BEFORE DELETING A RAW DATA FILE, THINK TWICE. All other file types can be produced again by the software from the RD file, but RD files can only be made by data collection.

  The full file specifier is displayed together with the question: (Y/N/G/Q).

  All versions of the file are presented one by one if there was no version number defined in the file specifier.

  The letters (Y/N/G/Q) indicate that you can choose Yes, No, Go, or Quit. If you choose:

  Yes - The defined file is deleted.
  If there are more versions of the file, then the next version is displayed, together with the choice (Y/N/G/Q).

  No - This version of the file is not deleted. The next version (if there is one) is displayed with the choice (Y/N/G/Q).

  Go - This version and - if applicable - all further versions of the file are deleted automatically.

  Quit - Neither this version, nor possible other versions of the file are deleted. The program returns to the menu.

- Rename a file, for instance a raw data file with lower version number can be given a new name, (not provided on Professional 350/380 version of APD1700).

- Tidy up the directory of files in a UFD. This command deletes optionally all A2, BK, SM, PK, MS, and 2D files. This is a convenient way of ´making room´ for new files.

- List a Directory (printed or displayed). A directory is a list of files present on a disk. A directory of a subset of files can also be requested (not provided with Professional 350/380 version of APD1700). The use of an asterisk (*) makes it easy to define a subset.

  An asterisk (*) ´wild card´ means put any character or group of characters in place of the asterisk. For instance: Filename: = "*.*" This means: Give a directory containing all the files on this disk (under this User File Directory).

  Also, "*.RD" means: all raw data files, and "TESTSA.*" means: all file types with the name TESTSA.

  "T*.RD" means: all raw data files starting with T.

  "TESTSA.RD;*" means: all versions of the file are taken.

  If you skip the version number the system takes as default the highest version number.

  If you enter version number ;0 the system will also take the highest number.

NOTE: RSX only recognizes octal version numbers.

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3.1 INTRODUCTION

The procedure to be used for instrument start-up depends on the computer configuration of the system. It is important to note that the first start-up after installation differs from all future routine starts.

```
* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
*                                                                               *
* CAUTION: All new RL discs are fitted with a "SHOCKWATCH" device just above    *
*          the handle. If this device shows RED, do not use the disc, as it     *
*          might damage the drive unit, contact your local representative.      *
*                                                                               *
* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
```

This chapter provides you with information that is specific to APD1700, the actual start-up procedure is described in Chapter 2 of the Software Instruction Manual. That chapter also provides information about ´Multi-user systems´, ´Logging in and out´, ´Switching off´ and ´Problems during start-up´.

3.2 FIRST-TIME START-UP

After the hardware has been completely installed and tested, a ´first-time´ start-up procedure as described in the Software Instruction Manual is followed. The main steps of this procedure are:

* Firstly a copy must be made of the ´master´ disk that you received (RL02 disks). This copying can be done in one of two possible ways, depending on what has been delivered:
  - If you received a combined disk containing the operating system (PW1211/xx) and the APD1700 analytical software (PW186x), then the copying is done by making a back-up copy of this ´master´ disk. Refer to the Software Instruction Manual.
  - If you received a disk containing only the APD1700 analytical software (PW186x), then the copying is done by transferring the APD programs to your system disk using the "GETAPD" routine. Refer to the relevant part of the Software Instruction Manual.

  Store the ´master´ disk in a safe place, it contains valuable extra files. On the work disk these files are deleted during the start up procedure to provide more space.

* If you received the software on floppy disks (MICRO/PDP-11 or Professional 350/380) first read in the floppy disks, refer to the Software Instruction Manual. Store the orginal set of floppy disks in a safe place.

Note that back-up copies of your work disks MUST be made at regular intervals, why and how this is done is described in the Software Instruction Manual Chapter 6. Also note that, if you have a PDF data base disk, you should make a back-up copy of it as soon as you have completed the First-time start-up, having copied it you should then use the copy as a work disk.

* Before the APD1700 program is installed, the operating system must function correctly and the terminal connections must be set up correctly. This means that if you received a PW1211 operating system, you must do the SETUPTRM procedure.

  NOTE: If you set up the terminals for the first time using SETUPTRM, or even changed existing terminal conditions using SETUPTRM, you must also change (inside the APD software) the SYSTEM PARAMETERS for Terminals. (SYSTEM PREPARATION, ASSEMBLE refer to Chapter 7.2.6.2).

* When the operating system is correctly installed you must then use the SETUPAPD program as described in the Software Instruction Manual. With this program, the actual location (device and UFD) of the APD1700 software is communicated to the system, and all the diffractometer connections are defined. If in the future you connect a new diffractometer to the system, or change the diffractometer connections, you can use the same program to define the ´new´ set up.

  NOTE: If you have defined new diffractometer connections for the first time using SETUPAPD, or even changed existing diffractometer connections using SETUPAPD, you must also change (or set up) the SYSTEM PARAMETERS for Diffractometers. (SYSTEM PREPARATION, ASSEMBLE refer to Chapter 7.2.6.3).

* The system is now ready for ´normal´ or routine start-up. An example of a complete first time start-up dialogue is given in the Software Instruction Manual.

* For the Professional 350/380 system a different procedure must be followed. Refer to the Software Instruction Manual.

3.3 ROUTINE START-UP; TO BOOT THE SYSTEM

For the Professional 350/380 the system is automatically started when "APD1700 P/OS version 3.0" is chosen from the "Additional Applications" menu. For all operating systems Chapter 2 of the Philips Software Instruction Manual describes how to start the system.

3.4 LOGGING IN AND OUT

Logging in and out of a PW1211 Operating System is described in the Software Instruction Manual Chapter 2.2.

- When the system then asks for a name or account, you type "APD" which is the name of the group of APD1700 users.

  Next the system requests a password: each APD user types his own password. On the APD1700 system disk four passwords have been prepared: APD, APD2, APD3, and APD4 respectively, together with the APD group name. Passwords and group names are described in more detail in Chapter 3.5 User(s).

  Passwords and group name can be changed (or new words chosen) using a special program (refer to the Software Instruction Manual Chapter 4.5). The single user probably will choose "APD" as his password. Because in doing so you will only have to type and remember the shortest word. Further, this password is the one suggested at the end of the system BOOT procedure.

  You will see that when entered, the passwords are not visible on the terminal screen or paper; they are not echoed by the computer. This feature is used for security reasons.

- The command, name, and password can be typed on one line: "LOG APD/APD" (or, for example: "HELLO APD/APD2").

  In this instance the password is visible at the terminal.

- The third method is a combination of the first two: after you type "LOG" answer the request for a name with "APD/APD".

The latter two ways of logging in are used in the examples in this manual.

After Logging in you can start the APD software package by typing "MCR APD".

When using a Professional 350/380 system you start by choosing "Additional Applications" in the P/OS main menu and after that choosing "APD1700 P/OS version 3.0" in the additional applications menu.

```
$LOG
Have a Good Afternoon
20-DEC-85 13:37 TT1:  logged off AMLIE6
>LOG APD/APD

RSX-11M BL35D  [1,54] System     AMLIE6
20-DEC-85 13:37 Logged on Terminal TT1:

Good Afternoon

>@LOGIN.CMD
;
; To start APD, type: MCR APD
;
>@ ^EOF
$
```

Figure 3.1 Logging Out and In under RSX

3.5 USER IDENTIFICATION CODE

Each PDP-11, MICRO/PDP or Professional 350/380 user has a two-number identification code that is used (with the password) for logging in. The code is in the form [g,m], with "g" being the user's group number and "m" being the user's member number. The brackets and comma are part of the code.

If you have a PW1211 operating system, you will find on your disk a number of accounts prepared for Logging in. If you have another operating system you will find prepared on the APD1700 disk (PW1867) the UFDs (space for your files) mentioned below.

For the PW1211 Operating System four accounts have been prepared on the distribution media, these are:

UIC[300,1] Prepared for the user with the group name APD and the password APD.

UIC[300,2] Prepared for the user with the group name APD and the password APD2.

UIC[300,3] Prepared for the user with the group name APD and the password APD3.

UIC[300,4] Prepared for the user with the group name APD and the password APD4.

If you have an RSX-11 or a Micro/RSX system you can prepare accounts using the "ACNT" program ("RUN $ACNT", refer to Software Instruction Manual Chapter 4.5).

In this way the APD group members can use each others files without hindrance (See note 1).

Each user's disk files are contained in a user file directory with the same code as his UIC. This code is part of the file specifier, for example: the APD user with password APD2 has UFD [300,2]. His raw data file TESTSA.RD (at DEVICE = disk unit DL0:) has the full specifier:

DL0:[300,2]TESTSA.RD

On the same disk is also prepared:

UIC[1,1] Name SYSTEM, password SYSTEM. You log in with this UFD in order to perform a number of high-privileged activities, such as Back-up and Set time.

The following directories are prepared on the APD distribution disk:

UFD[1,2] Contains the APD and RSX HELP files and the indirect command files (for example: @[1,2]BACKUP).

UIC[300,1] Prepared for the user with the group name APD and the password APD.

UIC[300,2] Prepared for the user with the group name APD and the password APD2.

UIC[300,3] Prepared for the user with the group name APD and the password APD3.

UIC[300,4] Prepared for the user with the group name APD and the password APD4.

UFD[300,20] These two UFDs are only used during installation (not for distri-
UFD[300,34] ution on floppy disks).

UFD[300,53] Small reference data base for test purposes.

UFD[300,54] Contains all APD program modules.

There are several other free UFDs, they are:

UFD[300,5] Not prepared but could be for APD/APD5.
UFD[300,6] Not prepared but could be for APD/APD6.
UFD[300,7] Not prepared but could be for APD/APD7.

UFD[300,60] You could use these numbers for a User reference data base. If more are required, use [300,61] to [300,67] and [300,70] to [300,77]. This is more fully described in Chapter 7.4.5.

UFD[300,160] You could use these numbers for DI files to be used as User patterns in the reference data bases. If more are required, use [300,161] to [300,177] and [300,156] and [300,157]. This is more fully described in Chapter 7.4.5.

Other UFDs free for any other use that you may have are:

UFD[300,100] to [300,177]
UFD[300,200] to [300,277]
UFD[300,300] to [300,377]

On the storage device of the reference data base (the PDF data base disk, normally DL1) you find:

UFD[300,57] Contains the Inorganic File, and

UFD[300,56] Contains the Organic File.

If more people want to use APD1700 on RSX or if you want to change a UIC, then new UICs, names and passwords can be prepared using the "ACNT" program ("RUN $ACNT", described in the Software Instruction Manual Chapter 4.5).

NOTE 1: Users from the same group can also Delete each others files. If required this can be restricted using the command "SET PROTECTION" (refer to the Software Instruction Manual Chapter 4.5).

For Micro/RSX the APD software does not allow the use of named directories, only numbered directories as described above.

With the Professional 350/380 there is only one user file directory (UFD) possible for the APD1700 user: [200, 200].

On a VAX/VMS system any UFD or subfile directory (SFD) can be chosen by a user.

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4.1 INTRODUCTION

Communication with the system software is via a menu dialogue for the ´main´ levels, and via a query dialogue for the ´lower´ levels.

After the system has been started up, and you have logged in; start the APD software package by typing "MCR APD" followed by "<CR>" for PW1211 (RSX-11 or Micro/RSX) systems. For Professional 350/380 (P/OS) systems choose "APD1700 P/OS Version 3.0" from the "Additional Applications" menu.

All instructions to the diffractometer system and all status reports and other messages from the system, are given in a conversation (dialogue) between you and the computer via the operator´s terminal.

In this operation manual, input or output on the terminal will be printed between quotation marks " ". All text normally printed between quotation marks " " is printed between single quotes ´ ´.

On the examples of actual dialogue the operator input is either shaded or underlined.

4.2 INPUT

Instructions can be given when the APD program displays the prompt symbol ":=".

All input is transferred to the computer when you press the (CARRIAGE) RETURN key "<CR>".

Commands and data can be input to the computer in one of two possible ways:

1. A ´menu´ of optional commands is presented on the display. A choice from the menu is made by typing the first character(s) of an option. In this way a route can be chosen towards the desired action or process.

2. A question and answer, or query dialogue is used in order to input parameter values for measurements or analyses.

4.2.1 CORRECTING TYPING ERRORS

IMPORTANT NOTE: NEVER USE THE BREAK KEY IN APD1700.

If an error has been made during input (for example a non-permitted command, or a parameter value outside the permissable range), a message may be issued by the system and the menu or question is re-displayed.

If you notice the error before the RETURN key is used, then you can erase the faulty characters. This is done on TEKTRONIX terminals using the RUB OUT key, on most other terminals the DELETE key, or the key marked should be used.

Use DELETE and the character immediately to the left of the cursor will be deleted. On DEC VT 100 and other video display terminals the character disappears and the cursor takes its place. On TEKTRONIX graphics terminals and printing terminals a backslash and the deleted character are displayed. If you press DELETE again the next character to the left will be deleted. When you have deleted what you wish, then type the correct input.

The BACK SPACE key should not be used, any input line including a BACK SPACE character will either be rejected or misinterpreted by the system.

4.2.2 DEFAULT ANSWERS

In all situations where it is useful and possible, a command or parameter value is proposed by the system. This is called the default value.

Default commands follow the ´normal´ sequence of events. Default values for parameters are chosen so that they are suited for most applications. Many of these defaults can be set in "Options/defaults", which appears in almost every menu. When the system asks for the defaults, sometimes the possibility "Optional" appears. This means that the system asks again that question at the proper time, and with the proposed command, that was specified in Options/defaults.

Example:

If you want most of your listings to be saved on a file, in order to use them again later on, or to have them printed on a daisy-wheel printer, the dialogue in Options/defaults is as follows:

"Listings to: Terminal, Printer, File, Optional:=". If "Optional" is chosen the system asks the next question:

"Default option: Terminal, Printer, File= Terminal:=" now "File" is chosen, and later on when the listing has to be made, the system again asks:

"Listing to: Terminal, Printer, File= File:="

If an existing list of parameters is changed, the last selected value is proposed as default.

If a proposed value or command (the default) is the required input, just give RETURN.

4.2.3 HELP TEXTS

If you are in doubt about which option to choose from the menu, you can ask the system for help. For each menu, one or more pages of information regarding the optional commands, and a reference to the appropriate chapter in this Operation Manual, can be requested by typing "?" (followed by the RETURN). In some cases the help facility can be used during query dialogue. For example:

> During the assembly of an analysis program the system requests "PROGRAM NUMBER :=". You can answer with "?", and an overview is then given of the program numbers already in use.

4.2.4 RETURN TO PREVIOUS MENU

You can return from any place in the menu to the previous menu level in one of three ways:

- A menu without a default choice only requires the RETURN key to return to the previous menu. A "/" (slash) can also be used.
- From a menu with default choice, you can return to the previous menu by giving a "/".
- From query dialogue you can return to the previous menu by typing "/" (which means acceptance of all further defaults in that query dialogue).On completion of a dialogue (the last question has been answered) the system automatically returns to the menu.

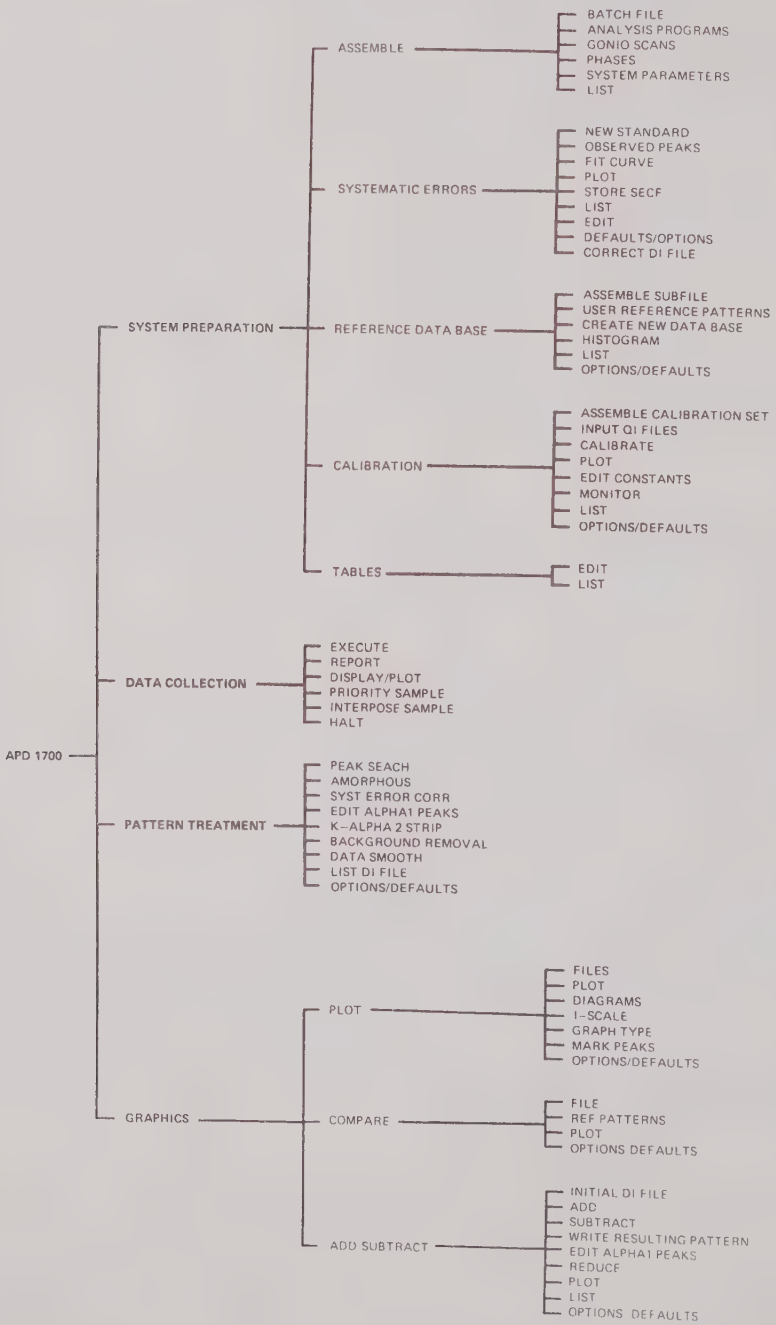
4.2.5 'FAST' INPUT

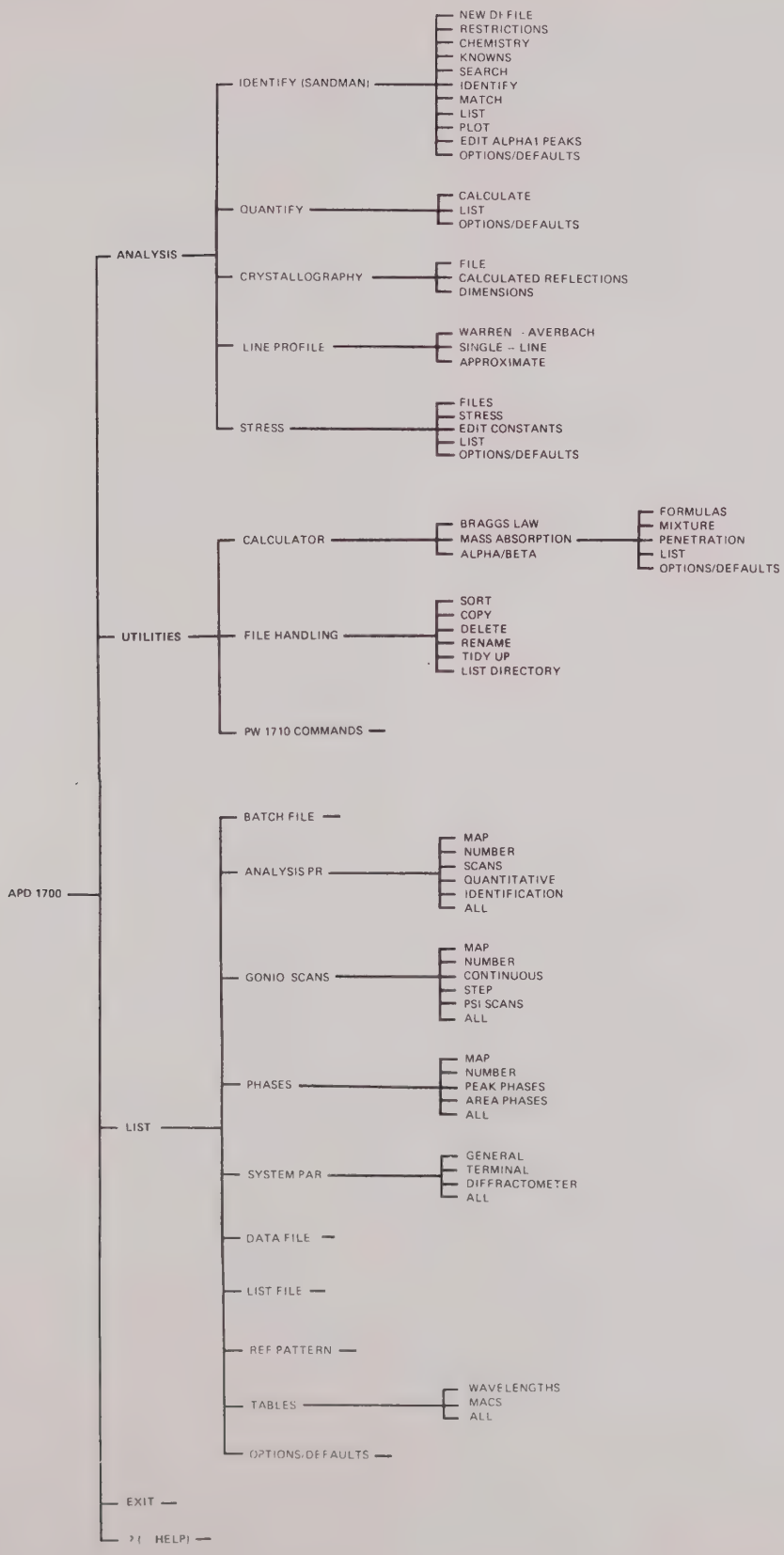
Instruction can also be given in a line (the individual instructions are separated by a comma "," and the input line is terminated with RETURN. The RETURN key causes the commands to be processed one after another.

If an error is detected somewhere in the command line, then the instructions following the error will be skipped, an error message is displayed, and the menu or parameter with the incorrect input is re-displayed.
A name or identification which contains a comma must be placed within single quotes (= inverted commas 'string'). An exception is the comma in the user identification code of a full file name (refer to the Software Instruction Manual Chapter 4.2 File specifier), for example DL0:[300,1]SAMPLE.RD.

NOTE: Leading and trailing spaces (spaces before and after a word or character) are eliminated by the system.

4.3 OVERVIEW OF COMMANDS IN THE APD1700 SOFTWARE




APD 1700
ANALYSIS
IDENTIFY (SANDMAN)
NEW DI FILE
RESTRICTIONS
CHEMISTRY
KNOWNS
SEARCH
IDENTIFY
MATCH
LIST
PLOT
EDIT ALPHA1 PEAKS
OPTIONS/DEFAULTS
QUANTIFY
CALCULATE
LIST
OPTIONS/DEFAULTS
CRYSTALLOGRAPHY
FILE
CALCULATED REFLECTIONS
DIMENSIONS
LINE PROFILE
WARREN - AVERBACH
SINGLE - LINE
APPROXIMATE
STRESS
FILES
STRESS
EDIT CONSTANTS
LIST
OPTIONS/DEFAULTS
UTILITIES
CALCULATOR
BRAGGS LAW
MASS ABSORPTION
FORMULAS
MIXTURE
PENETRATION
LIST
OPTIONS/DEFAULTS
ALPHA/BETA
FILE HANDLING
SORT
COPY
DELETE
RENAME
TIDY UP
LIST DIRECTORY
PW 1710 COMMANDS
LIST
BATCH FILE
ANALYSIS PR
MAP
NUMBER
SCANS
QUANTITATIVE
IDENTIFICATION
ALL
GONIO SCANS
MAP
NUMBER
CONTINUOUS
STEP
PSI SCANS
ALL
PHASES
MAP
NUMBER
PEAK PHASES
AREA PHASES
ALL
SYSTEM PAR
GENERAL
TERMINAL
DIFFRACTOMETER
ALL
DATA FILE
LIST FILE
REF PATTERN
TABLES
WAVELENGTHS
MACS
ALL
OPTIONS/DEFAULTS
EXIT
?(HELP)

4.4 EXAMPLES OF INPUT/OUTPUT

After the APD program has been started the main menu is displayed. To prepare the system, and assemble an analysis program (for example: number 43):
'normal' procedure:

```
PHILIPS APD1700 AUTOMATED POWDER DIFFRACTION              24-JAN-86  12:45

SYSTEM PREPARATION, DATA COLLECTION, PATTERN TREATMENT,
GRAPHICS, ANALYSIS, UTILITIES, LIST, EXIT, ? (= HELP) := S

SYSTEM PREPARATION                                       24-JAN-86  12:45

ASSEMBLE, SYSTEMATIC ERRORS,
REFERENCE DATA BASE, CALIBRATION, TABLES := A

ASSEMBLE PARAMETER FILES                                 24-JAN-86  12:45

BATCH FILE, ANALYSIS PROGRAMS,
GONIO SCANS, PHASES, SYSTEM PARAMETERS, LIST := A

Diffractometer system number = 1 :=

Assemble analysis program number := 43

New analysis program:  43

Program name (max 20 chars) =                          :=
```

'fast' input:

```
PHILIPS APD1700 AUTOMATED POWDER DIFFRACTION              24-JAN-86  12:46

SYSTEM PREPARATION, DATA COLLECTION, PATTERN TREATMENT,
GRAPHICS, ANALYSIS, UTILITIES, LIST, EXIT, ? (= HELP) := S;A;A;;43

SYSTEM PREPARATION                                       24-JAN-86  12:46

ASSEMBLE, SYSTEMATIC ERRORS,
REFERENCE DATA BASE, CALIBRATION, TABLES  = A

ASSEMBLE PARAMETER FILES                                 24-JAN-86  12:46

BATCH FILE, ANALYSIS PROGRAMS,
GONIO SCANS, PHASES, SYSTEM PARAMETERS, LIST  = A

Diffractometer system number = 1  =

Assemble analysis program number  = 43

New analysis program:  43

Program name (max 20 chars) =                          :=
```

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5.1 PERIPHERALS

A peripheral is a device, that can either provide the system with input (commands, instructions, and so on) or accept output from it. Terminals, (line) printers and plotters are peripheral devices. Disks are also peripherals, but because they become part of the computer system when installed we do not discuss them in this chapter.

5.2 TERMINALS

A terminal is a hardware device with two functions: sending input to the operating system and receiving output from the operating system. Terminal input usually comes from a typewriter-style keyboard. Output appears on terminals in one of two ways, depending on the terminal type:

- Printing terminals provide a permanent record of the output on paper.
- Video terminals have a video screen for receiving output. In the APD1700 system we distinguish between alpha-numerical video terminals and graphics terminals.

On the paper or screen you seem to see the ´input´ that you have given via the keyboard. This is however also output from the computer, because the system echoes each input except for the password during log in.

The computer also treats each diffractometer (connected via its PW1710 controller) as a terminal.

The special properties of the different terminal types require attention during connection and when assembling System Parameters. Refer to the Software Instruction manual for setting-up information for the preferred terminals.

When a Professional 350/380 computer is used a graphics terminal is incorporated in the system. The system can have a printer connected to provide a hard copy printout of the screen output, but the same printer can be used as the ´system printer´ in the APD1700 programs.

5.2.1 PRINTING TERMINAL

A printing terminal is the ideal operator terminal for a system which performs analyses routinely. This type of use requires one time only input to start the analysis, and hard-copy output to report the results during unattended operation.

Printing terminals are not very well suited for typical interactive use: they are relatively slow, and paper consuming during dialogue. In most cases it is connected and used as the system printer (refer to Chapter 5.3). Baudrate is normally 9600, and line width often up to 132 characters.

5.2.2 VIDEO TERMINAL

A video terminal (also called: CRT or VDU) is the ideal terminal for dialogue: it is fast and silent, and does not produce piles of paper.

Listings of files, and other output from which a hard copy is required, can be sent to the system printer or to a (graphics) terminal with hard copy unit. Baudrate 9600 and 80 characters line width is normal.

5.2.3 GRAPHICS TERMINAL

This is the most useful type of terminal, as it can produce graphical images of the measurements and analysis results.

Dialogue, graphics output and listings can be made on this type of terminal if a hard copy facility is available. The APD1700 system has been designed with graphics terminal very much in mind.

Tektronix graphics terminals equipped with hard copiers give a copy of the screen if you press the (HARD) COPY key. The Hewlett Packard graphics terminal 2623A has one key for hard copies of graphics: the GRAPH COPY key, hard copies of text are made using the function keys (f1 to f8). Press AIDS and f1 (DEVICE CONTROL), and then you can make copies of any part of the 48 lines of text in the internal buffer. Use the keys f4 to f8 together with the ROLL DOWN and ROLL UP keys and the arrow (cursor) keys underneath f5 to f7.

The Hewlett Packard graphics terminal 2648A can make copies on (for example) a HP2631G external printer. In the APD1700 software the following functions are programmed for the function keys f1 to f4:

f1: Graphics to printer
f2: Alpha-numerics to printer
f3: Page feed on printer
f4: Two line feeds on printer

If you have a Professional 350/380 system with a printer connected (usually LA50), the screen that is displayed on the terminal can be printed on the printer by pressing the PRINT SCREEN key.

Baudrate is usually 9600, but for the HP 2648A terminal, 2400 baud is the maximum. The number of characters per line depends on character size: line width is chosen by the system when you define character size with terminal type.

5.2.3.1 Hardware Set-up of Graphics Terminals and Plotters

All APD graphics programs are based on TEKTRONIX (or Tektronix compatible) terminals and Philips or Tektronix plotters. In order for the plot programs to function properly, especially the interactive cursor mode, the terminals and the plotters must be installed correctly. For Philips plotters refer to the Software Instruction Manual. For other graphics terminals and plotters information about the set-up or setting up of terminal parameters (strapping) is given in the individual terminal/plotter manuals.

The following terminal parameters must be set as indicated:

- RUBOUT (DEL): DEL in the LOY position.
  Within the Tektronix, this enables the terminal to interpret the RUBOUT (DEL) key as Low Order Y code.
- GIN terminators: None.
  This parameter is sometimes called "End of a line string". These are terminating characters that are sent to the computer after transmission of the cursor position when the system is in interactive cursor mode.

Depending on the terminal model, some additional parameters must be set:

- Bypass cancel character: NUL.
  The cursor information sent from the terminal to the computer will not be echoed by the computer. Therefore the terminal must not wait for a "Bypass cancel character".
- Prompt character (string): Empty.
- End-of-message (EOM) character (string): NUL.

Terminals of the TEKTRONIX 41xx series have to be 'set up' with CODE TEK. Other terminal models must be set up by means of hardware or software straps on the terminal itself.

When you do not have a Professional 350/380 system, you have to define the terminal type within APD1700 via the commands ASSEMBLE, SYSTEM PARAMETERS (SYSTEM PREPARATION). Refer to Chapter 7.2.6.2. For TEKTRONIX compatible terminals that are not listed in the menu, we advise you to enter "4010/12" type.

The strapping of certain of the recommended terminals is described in the Software Instruction Manual.

5.3 SYSTEM PRINTER

The system printer is in most cases a (fast) printing terminal which is connected to be controlled by the Queue Manager (refer to Chapter 7.2.6.1).

Each user of the system, and the system itself (for example Data Collection) can direct listings of results, log files and messages to the same printer. Each list waits for its 'turn' in the queue.

We advise using one printing device as the system printer. Baudrate is normally 9600, width 132 characters.

5.4 PLOTTER

A multi-colour plotter can be used as part of the system. We advise that the plotter is connected to the system via the Queue Manager (refer to Chapter 7.2.6.1), except for Professional 350/380 systems. After a plot command has been given, the plotter starts and the terminal is free for further dialogue. Several users can have plots made, each in turn, while others wait in the queue. In this case it is convenient if the plotter has a paper transport facility.

If there is no terminal connection free for the plotter, it can be connected in 'parallel' to a terminal. In this case plots can be requested from this terminal only, and the terminal is not free as long as the plotter is busy. The baudrate depends on the model, a Philips PM8151 can be used at its maximum transmission speed: 2400 baud. The Philips PM8154 and the Tektronix plotter model 4663 can be used at the maximum speed of 9600 baud.

For Professional 350/380 systems a Hewlett Packard plotter must be used; for connection and baudrate, refer to the Professional manual.

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6.1 INTRODUCTION

This chapter describes the software programs necessary for the preparation, execution, and evaluation of x-ray diffraction experiments. In other words: it describes the commands of the ADP1700 main menu with which the analytical programs are chosen/activated. A short description of each of the main programs is given. Chapters 7 to 13 explain in detail the principles and use of each of these main programs together with the programs and sub-programs that are accessable through them.

6.2 SHORT DESCRIPTION OF THE MAIN PROGRAMS

6.2.1 SYSTEM PREPARATION

Before any data collection, data treatment, or analysis can be done, the system has to be prepared: by means of manual (keyboard) input of measurement and calculation parameters, by correction of goniometer angles for systematic errors, by editing reference data bases for phase identification, and by determination of calibration constants for quantitative analysis.

- The REFERENCE DATA BASE program is an optional extension (PW1862) to the APD kernel package (PW1867).

- The CALIBRATION program is part of the QUANTITATIVE ANALYSIS option (PW1863).

More information about system preparation is given in Chapter 7.

6.2.2 DATA COLLECTION

This program enables the execution of data collection on either a single sample, or a batch of samples. The measurement on a priority, and interposing the measurement on a sample, is also possible. The program enables a report to be made on the status of ongoing experiments; and it can be used to halt experiments on one or more diffractometers.

The DATA COLLECTION module (PW1866) is not available for the VAX computer. It is assumed that the diffractometer system(s) are connected to a PDP-11, a MICRO/PDP-11, or a Professional 350/380 series computer.

Details of this program are given in Chapter 8.

6.2.3 PATTERN TREATMENT

This program enables you to do the following:

- Peak Search on RD, SM and A2 files
- Peak Search for amorphous maxima in BK files
- Correct a DI file for systematic errors
- Edit the K-alpha$_1$ peaks of a DI file
- Strip the K-alpha$_2$ contribution from an RD file
- Remove the background from an RD or SM file
- Smooth the data in a raw data file
- List DI files

Details of this program are given in Chapter 9.

6.2.4 GRAPHICS

This program enables measurement results (RD files) and/or intermediate results (for example: DI files) to be drawn on a graphics terminal or a digital plotter for visual evaluation/interpretation. It is also possible with this program to compare raw data files with each other, with DI files or with reference patterns. DI files and/or reference patterns can be added to or subtracted from each other.

When using this program, a graphics cursor can be used as an aid during evaluation and/or editing, or to 'highlight' certain features and enter text to the plot.

Details of this program are given in Chapter 10.

6.2.5 ANALYSIS

Up to five (optional) programs can be used to analyse data that has been collected. These programs are:

- Phase identification (search-match PW1861)
- Quantitative analysis (PW1863)
- Crystallographic analysis (PW1865)
- Line profile analysis (PW1864)
- Stress analysis (PW1868)

The results of one type of analysis program may well be used as an aid in another analysis program.

NOTE: The APD1700 Software Package provides you with programs to aid you in the analysis of phases and phase mixtures. Some analyses may be solved automatically by the program, while other analyses may required operator interaction. A sound knowledge of diffractometry is necessary to evaluate the results, see the references in paragraph 6.3.

Details of each of these programs are given in Chapter 11.

6.2.6 UTILITIES

Utilities are a set of auxiliary programs for various purposes:

- A facility to perform diffractometry related calculations.
- Disc file handling.
- The ability to use the PW1710 microprocessor directly.

Details of these programs are given in Chapter 12.

6.2.7 LIST

This program can provide a listing on your terminal (or the system printer) of each parameter file that has been assembled, and/or a listing of each data file or reference pattern, or a listing of the wavelength tables and/or mass absorption coefficients. It is possible to partially list parameter files. Data files can be partially or completely printed or displayed, using restrictions described in the data treatment/analysis Chapters.

Details of this command are given in Chapter 13.

6.2.8 EXIT

When you select this command the system leaves the APD main menu so that you can use other programs or the operating system's facilities, or you can logout or shutdown the system. It is not possible to use the command during data collection.

6.2.9 ? (HELP)

Helpful information is available for each menu, and at many places during dialogue. The help text will be displayed when you type "?".

More information about the Help is given in Chapter 4.2.

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7.1 INTRODUCTION

Before any data collection, data treatment, or analysis can be done, the system has to be prepared: by means of manual (keyboard) input of measurement and calculation parameters, by correction of goniometer angles for systematic errors, by editing reference data bases for phase identification, by determination of calibration constants for quantitative analysis.

The REFERENCE DATA BASE and CALIBRATION programs are not part of the APD kernel program, they can be ordered/purchased separately with their own type numbers:

- REFERENCE DATA BASE has the type number PW1862
- CALIBRATION is part of the QUANTITIVE ANALYSIS program PW1863.

7.2 ASSEMBLE PARAMETER FILES

7.2.1 INTRODUCTION

Before measurements, analyses or calculations can be made, the system has to be supplied with the parameter values necessary for performing those tasks. Therefore you have to assemble parameter files.

The parameters are divided into groups according to their purposes, they are:

* System parameters: which are about the computer system, the terminals, and the diffractometer system(s). Some of these parameters are for information only (for example: during printout), and some of them actually control the system (for example: Upper and Lower levels of the Pulse Height Discriminator).

* Goniometer scans: which describe the measurement parameters for scans that you will require the goniometer to make to provide you with the RD files for phase identification, crystallographic, line profile, and stress analysis.

* Phases: describe the parameters for the measurement of diffraction profiles to provide you with the QI files for quantitative analysis.

* Analysis programs: connect measurements (scans or phases) to data treatment, calculations, and final analysis.

* Batch file: which is used when more than one sample is to be processed, or when one sample has to be analysed with several programs. The batch file is used to gather together all the parameters and data that are required for each sample.

Each APD user has his own set of files that contain the parameters for measurements and analyses, these files are within his own UFD (in [200,200] if you have a Professional 350/380) and are as follows:

APDANA.DAT for analysis programs

APDANA.D01 to D03 for quantitive analysis, calculation

APDANA.D10 and D11 for automatic peak search and identification procedures

APDPHA.DAT for phases

APDSCN.DAT for goniometer scans

If a system has more than one diffractometer, there are more sets of these files, one set for each diffractometer. For example: if one user had three diffractometers, he or she would have three sets of analysis programs: APDANA.DAT, APDANA2.DAT and APDANA3.DAT. A user can copy a file from another user if he wants to work with the same parameters. For more information about the contents of the Parameter files refer to Chapter 2.2.

Measurements are started with the Data collection program. Data collection on one sample is done by entering the required Analysis program number. Data collection on a number of samples (either in a sample changer magazine or not) is done using a Batch file. In a Batch file the required Analysis program numbers are defined for one or more groups of samples.

Analysis programs can specify (per diffractometer system):
- To perform a number of goniometer scans, for graphics display or stress analysis.
- To perform a quantitative analysis: data collection plus calculation.
- To make a scan for the purpose of phase identification, crystallographic or line profile analysis. In a phase identification, the data collection, plus peak search, plus identification can be performed.

There is only one System parameter file (LB0:[1,2]APDSYS.DAT) per APD system. Each user reads and uses the same basic parameters from this file. If there is more than one APD user for a system, they should discuss changes that have to be made to the System parameters. In general it is advisable in such situations that the users appoint one of the users as the 'system supervisor' who manages the System parameters.

7.2.2 BATCH FILES

A batch file contains the instructions for data collection and analysis if more than one sample has to be analysed and/or more than one type of analysis has to be applied to a sample or to (a) group(s) of samples.

A batch file can be used for samples in a sample changer magazine, but also in a diffractometer system without a sample changer. In the latter case the samples are inserted manually in the sequence of the 'position numbers'.

There are several ways in which samples can be combined with analysis programs in batch files:

* Up to 42 samples can all be measured by the same analysis program.
* Up to 42 samples can all be measured by different analysis programs.
* Groups of samples and/or single samples can be measured with different combinations of analysis programs.
* Any one sample may be included in more than one group.

When you assemble a batch file, the file type extension is always "JB" for the first diffractometer in a system, and then from the second onwards the extension is "JB2", "JB3" and so on.

7.2.2.1 Assembling Batch Files

To assemble a batch file you must give "B" in the ASSEMBLE PARAMETER FILES mode, give the number of the diffractometer system (if more than one defined, the system will automatically use analysis programs designed for the selected diffractometer system), and the system will request a name for the batch file. Now you can do one of three things:

A. Type an existing file name. This allows you to accept, change or delete the file with that name.

B. Type a 'new' file name. This will open a new batch file.

C. Type "?" in place of the name. This will cause a list of existing batch file names to be displayed by the system.

- Next you have to define whether the raw data file names for each individual sample are to be entered by you or are to be generated automatically by the system. A raw data file name is given to every sample in a batch file, the system asks whether or not you wish to name the raw data files yourself by asking "Raw data file name generation: Individual, Automatic". You can choose:

  Individual, which means that you will choose the first six characters in every raw data file name.

  Automatic, which means that all the raw data files will have the same first three characters, followed by the sample number.

  If the batch file contains more than one job, the raw data files for samples in that batch are named as follows:

  1. The first job produces a file name of (up to) six characters.
  2. The following and subsequent jobs produce a file name of (up to) six characters followed by a job number suffix starting at J02 up to J42.

  If you choose individual file names, then the system requests a sample identification of maximum 20 characters. If you give RETURN only, then the system suggests for the raw data file name the first three characters of the batch file name, followed by sample position number and job number. For example: "EXA<S01><J02>" for batch file "EXAMPL.JB". You can choose a different name if you want to (only the part "<J02>" remains the same).

  If you enter a sample identification, then the system suggests the first six alpha-numerical characters (followed by the job number) for the raw data file name:
  "TESTSA<J03>" for sample "TEST - SAMPLE".

  If you choose automatic file name generation you can still change the file name because the system requests the first characters for the file names, the first three characters of the batch file name are default. Example: "Raw data file name prefix = EXA :=". You can choose up to three other characters, the system completes the file names by adding the sample number (and the job number). This makes it possible for routine analysis to change the raw data file names for each new batch of samples but still work with the same batch file name for data collection. You can leave the contents of the batch file unchanged by giving "/" after the request "Job number = 1 :=".

- The system requests the Job number. In the job you specify which samples are to be measured by a particular analysis program, if, for example: a sample is to be measured by three analysis programs, three jobs are necessary. Samples can be analysed by several analysis programs by including their position number in more than one job. In an existing batch file you can choose any existing job with the purpose of changing it. For new jobs you can only take the lowest free number. If you enter a higher number, the system repeats the question with the first free number as proposed value.

  If you enter "?" then the system displays:

  "Next free job number = 3", and repeats the question with this number as proposed value: "Job number = 3 :=".

Next the system requests the position (or sequence) number of the first and the last sample of this group. If there is only one sample to be analysed in this job, then enter the same numbers for first and last sample position.

Next the analysis program to be applied to the samples in this job must be defined. If you enter the number of an analysis program which has not yet been assembled, then the system displays "Analysis program has not been assembled". If this message is displayed, take care to assemble this program before you start Data collection.

After you have specified the analysis program number, the system asks if you wish to change any of the system parameters. Several of the parameter values can be chosen to be different from the values in the System parameter file, during the execution of this job, these parameter are:

PW1710 display: left
PW1710 display: right
PHD lower and upper level
Recorder on: Yes, No
Ratemeter full scale
Ratemeter time constant
Recorder speed
Sample spinning: Yes, No

Depending on the type of analysis program, additional sample information may be requested by the system. For example, for Quantitative analysis, if it has been specified in the analysis program that sample specific information should be entered at sample introduction, that information can be entered now:

- Internal standard model: the weight fraction of the internal standard material.
- Binary and Matrix flushing models: the total of analytes (weight fraction).
- General model: mass absorption coefficient (cm^2/g).

The sequence in which this information is entered is as follows:

- The first information that will be requested, will be for the samples in this job for which no information has been previously entered.

- Then the information for all the samples in this job is displayed. The system asks whether or not this information is to be changed. By entering the sample number(s) you can change the sample specific information for one (or more) samples.

NOTE: Only one value for "Internal Standard", "Total of analytes", and/or "Mass absorption coefficient" can be stored within a batch file for each sample. It is therefore not possible, for example, to use several analysis programs on one sample if different internal standard phases have been defined in those programs. If you want to do this you have to assemble another batch file.

The dialogue is halted by entering "/" instead of a job number, when the system requests one.

7.2.3 ANALYSIS PROGRAM

The analysis program is the program that you select to control the actual collection and treatment of data, and for the analysis of the results.

When you are in the Data Collection mode, you will be asked by the system to provide an analysis program number (or a batch file name to connect analysis programs to samples and sample identifiers) before the system starts data collection.

7.2.3.1 Assembling Analysis Programs

You can enter the Assemble analysis program mode by giving "A" in the ASSEMBLE PARAMETER FILES mode.

Firstly the system requests the diffractometer system number (if more than one is defined). Each analysis program is designed for one diffractometer system and must therefore only contain scans or phases that were assembled for that diffractometer system.

Next the system asks for the analysis program number. If you enter "?", an overview of the existing program numbers is displayed. If you give RETURN, the system chooses the next available free number for you. If you enter an existing program number, then the contents of that program will be displayed, followed by the options: ACCEPT, CHANGE, DELETE = CHANGE := .

If you enter a "/" or "A", the program is left as it is and the system asks for the next analysis program number. If you enter another "/" you return to the Assemble menu.

If you choose CHANGE, then all questions will be repeated with the existing answers as proposed answers.

A program name of 20 characters maximum can be used to indicate the purpose of the program.

You can choose any one of three types of analysis program, they are:

- Scans only
- Quantitative analysis
- Identification

These analysis program types are described in the following paragraphs 7.2.3.2 to 7.2.3.4.

7.2.3.2 Scans Only

You choose this type of analysis program when you require data collection for stress analysis or for graphics display only, it offers the possibility to perform (up to 55) goniometer scans on a sample and have the results stored in one RD file.

When you choose Scans only ("S") the system will request "Scan number :=". You must enter the numbers of the goniometer scans that you want. When no more scan numbers have to be added, give RETURN to terminate the assembly of the analysis program.

The results of the goniometer scans (a ´multiple´ RD file) can be used for subsequent visual evaluation (refer to Chapter 10, Graphics), or stress analysis if Psi scans were defined in the program (refer to Chapter 11.6, Stress Analysis).

The goniometer scans specified in the analysis program must have been assembled before that program can be executed in the Data Collection mode. This is done with the "Assemble, Gonio. scans" command as described in Section 7.2.4.

If you have entered more than the permitted limit of 55 scans the system will display "More than 55 scans specified".

7.2.3.3 Quantitative Analysis

This type of analysis program provides a ´complete´ automatic analysis procedure consisting of: the collection of data, the calculation of net intensities, and the establishment of weight concentrations. The results of up to 25 analytical phases per sample are stored in one QI file.

The gross intensity of each phase can be corrected for background and (up to 4) overlapping phases (refer to Chapter 11.3.3).

The number of phases (analytical plus overlapping) in one analysis program may not exceed 55.

Before you can use an analysis program for "Data collection, Execute", you must first assemble the phases that are contained in that program. Use the "Assemble, Phases" as described in section 7.2.5. After that the calibration constants of the phases must be established with the "Calibration" program as described in section 7.5.

When you choose Quantitative analysis "Q" the system will request:

"Model: General, Straight line, Addition, Internal standard, Matrix flushing, Binary, External monitor, Thin Sample, := "

The following paragraphs provide a summary of the different calculation models and intensity correction procedures (for background and line overlap), they are described in detail in Chapter 11.3. The formulas in this summary use the following notation:

B_i	:	Calibration constant of phase i
B_{im}	:	Mass calibration constant of phase i
C_i	:	Concentration of analytical phase i
C_s, B_s, I_s	:	Concentration, calibration constant and intensity of internal standard phase
I_i	:	Net intensity of phase i
F_m	:	Thin sample mass absorption factor
MAC	:	Mass absorption coefficient of sample (mixture)
MAC_i	:	Mass absorption coefficient of phase i
M_i	:	Mass of analytical phase i
SUM	:	Sum of products (BI) for all analytical phases
S	:	Total concentration of analytical phases (Sum)

Concentrations of phases will be displayed as and must be entered as weight fractions.

7.2.3.3.1 Summary of Quantitative Analysis Models

The different calculation models that you can use in Quantitative analysis are described in detail in Chapter 11.3, this section provides a short description of each of the models together with a description of the dialogue necessary to incorporate that model into the Quantitative Analysis program.

General, formula : $C_i = B_i.I_i.MAC$

This model can be used if the Mass absorption coefficient of the sample is known; for calibration standards as well as for ´unknown´ samples.

Enter the numbers of the analytical phases, and if applicable: the background correction and overlapping phase numbers. When no more phases have to be entered give RETURN.

The system will request:
"Constant mass absorption coefficient? Yes, No = No := ".
If you enter "No", the system wil display:
"MAC will be requested at sample introduction".
If you enter "Yes", you will be asked to enter the value of the mass absorption coefficient. This method can be used if the MAC for all samples is a constant, or if you analyse samples with a narrow concentration range where you may assume the absorption to be constant. Alternatively you could use the straight line model.
Finally the system requests:
"Ratio to monitor? Yes, No = No := ".
It is advisable to use the monitor ratio method to compensate for instrumental intensity changes. If you type "Yes", don´t forget to assemble an analysis program of the External monitor model. Measure the monitor sample before the calibration standards or the unknown samples.

Straight line, formula : $C_i = B´_i.I_i \quad (B´_i = B_i.MAC_i)$

This calculation model can be used if the mass absorption coefficient is a constant, or if the concentration range is so small that MAC is practically constant. It is an alternative to the General, constant MAC model.

Enter the numbers of the analytical phases, and if applicable: the background correction and overlapping phase numbers. When no more phases have to be entered give RETURN.

Finally the system requests:
"Ratio to monitor? Yes, No = No := ".
It is advisable to use the monitor ratio method to compensate for instrumental intensity changes. If you type "Yes", don't forget to assemble an analysis program of the External monitor model. Measure the monitor sample before the calibration standards or the unknown samples.

Addition, formula: $C_1 = \frac{R_1}{R_2 - R_1} \cdot a_2$

With $R_i = I_{ai}/I_{ri}$
i = measurement numbers, sample 1 is the original sample (in other words: $a_1 = 0$)
a = added fraction of analytical phase
I_a = intensity of analytical phase
I_r = intensity of reference phase

This calculation model uses the fact that if a known fraction of the analytical phase is added to a sample, the intensity of the analytical phase raises and at the same time the intensity of the reference phase diminishes. No calibration is needed with this model.

Internal standard, formula : $C_i = \frac{B_i}{B_s} \cdot \frac{I_i}{I_s} \cdot C_s$

With this calculation model you can eliminate the influence of the absorption by adding (and carefully mixing) an amount of internal standard material to each sample, calibration standards as well as unknowns.

Firstly, enter the phase number of the internal standard, then the analytical phases, and if applicable: the background correction and overlapping phase numbers. When no more phases have to be entered give RETURN.

Then the system requests:
"Fixed concentration of internal standard? Yes, No = No:= ".
If you enter "Yes", then you are requested to enter the concentration of the internal standard: "Concentration (fraction)= 1.000 :=". The fixed concentration must thereafter always be weighed precisely for all following samples, calibration standards as well as the unknown samples.

In most cases it is better to choose "No", and then the system displays:
"Concentration will be requested at sample introduction".

Matrix flushing, formula : $C_i = \frac{B_i \cdot I_i}{\text{SUM } (B.I)} \cdot S$

In this model the influence of the absorption is 'flushed out' of the formula by using the sum of the analytical phases.

If you don't know the total concentration (for example, because of an amorphous component), you will still receive the 'relative amounts' of the analytical phases as a result.

Enter the numbers of the analytical phases, and if applicable: the background correction and overlapping phase numbers. When no more phases have to be entered give RETURN.

The system will request :
"Total of analytes known? Yes, No, At introduction = At introduction:=".
If you enter "No", then the system displays:
"Total of analytes (fraction) will be set to 1.0".

If you enter "Yes", then the system requests:
"Total concentration of analytes (fraction) = 1.000 := ". You may enter any number up to 1.0000.

If you enter "At introduction", then the system displays:
"Total of analytes will be requested at sample introduction".

Binary, formula : $C_i = \frac{1}{1 + \frac{B_j}{B_i} \cdot \frac{I_j}{I_i}} \cdot S$

This model is a special case of matrix flushing, only for two analytical phases (i and j).

After you have entered the numbers of the analytical phases, and if applicable: the background correction and overlapping phase numbers, the system requests:

"Total of analytes known? Yes, No, At introduction = At introduction:=".
If you enter "No", then the system displays:
"Total of analytes (fraction) will be set to 1.0".

If you enter "Yes", then the system requests:
"Total concentration of analytes (fraction) = 1.000 := ". You may enter any number up to 1.0000.

If you enter "At introduction", then the system displays:
"Total of analytes will be requested at sample introduction".

External monitor.

This type of program is not for the analysis of an unknown sample, but for establishing the intensity of an external monitor sample. This intensity is stored and used for the correction of intensities of samples analysed with the model General, Straight line or Thin sample (if required).

The monitor phase number must be entered.

Thin sample

This model can be used for mass calculation of samples that contain very little powder, such as air deposited dust samples (measurement of air pollution) or samples of which only a few crystals are available. Also concentration calculation according to the General, Straight line, Internal Standard, Matrix flushing or Binary models can be performed.

Mass formula: $M_i = I_i \cdot F_m \cdot B_{im}$

with M_i = mass of compound i
I_i = intensity of infinitely thick sample (converted from thin sample intensity)
F_m = thin sample mass absorption factor
B_{im} = mass calibration constant of compound i

The system first asks if you want to do a Concentration calculation, a Mass concentration or a Plate measurement only.

When Concentration or Mass calculation is chosen the system asks if the plate reference phase is Universal, Individual or None. If you specify a plate reference phase the system asks if you want to use the ratio to Monitor. Thereafter the dialogue for Concentration calculation proceeds according to the dialogue belonging to the model used.

When Mass calculation is chosen the system asks for the analytical phases, with their background and overlapping phases.

When Plate measurement only is chosen the system only asks the plate reference phase number.

NOTE: Calibration for the concentration calculation models have to be done with infinitely thick samples, because otherwise the accuracy will be diminished.

If you are changing an existing quantitative analysis program and you enter "/" for the analytical phase number, the system skips the following analytical phases and continues with the sample dependent information, like:

- Mass absorption coefficient
- Monitor ratio
- Concentration of internal standard
- Total concentration of analytes

When you finish assembling an analysis program, one or more error messages may be displayed by the system. If any of the messages are displayed, you must take the action that we suggest in the following text, otherwise the analysis program will not give satisfactory results. In order to make these suggested corrections you should complete the analysis program using the change command. These messages are:

"No analytical phases specified". All models (except External monitor).
You have to enter analytical phase numbers.

"No internal standard phase specified". Internal standard model.
Enter the phase number of the internal standard.

"No monitor phase specified". Monitor mode.
You have to enter the phase number of the external monitor.

"Overlap correction of phases i and j to each other". All models except for External monitor model. You specified phase i for overlap correction of phase j, and phase j to correct phase i, this is mathematically impossible. Choose another peak for phase i or phase j.

"Overlap correction of phase number i to itself". All models.
You specified phase i for overlap correction of phase i. Enter another phase number.

"More than 55 phases specified". All models except for Binary and External monitor.
Find a peak with less overlapping phases for one or more of the analytical phases.

The following warning may be displayed by the system:

"The following phases have not been assembled:
ii jj ".

If this message is displayed, you must not forget to assemble these phases before starting data collection with this analysis program.

7.2.3.4 Identification

With this type of analysis program, data collection consists of one goniometer scan, designed for subsequent phase identification. The scan has to be assembled separately using "Assemble, Gonio scan" (refer to Chapter 7.2.4).

It is possible to do Peak search and phase identification immediately after Data collection as an automatic analysis procedure. You can change the parameters specified in Options/Defaults of Pattern Treatment (except for K-alpha 2 strip, refer to Chapter 9.2) and Identify (Sandman) (except for Knowns, refer to Chapter 11.2.3). You can also specify a Restrictions Subfile, a Chemistry Subfile and Known phases (refer to Sections 7.4.2, 11.2.6 and 11.2,13.4.). If you want to do a Systematic Error Correction (refer to Chapter 7.3.) or Crystallographic analysis (refer to Chapter 11.5) after Peak Search you can omit the Identification.

If you have specified one or more known phases the system will perform a residual search, otherwise a search for major phases will be done (refer to Chapter 11.2.7).

It is also possible to do all this interactively after Data Collection, in which case you can also use the Graphics commands (refer to Chapter 10) and/or $Alpha_2$ stripping (refer to Chapter 9.2).

7.2.4 GONIOMETER SCANS

Step scans and continuous scans contain the parameters for collection of data for Identification, Crystallographic, or Line profile analysis or Scans only, Psi scans are used for Stress analysis. You can enter the Assemble goniometer scans mode by giving "G" in the ASSEMBLE PARAMETER FILES mode. First, if more than one diffraction system has been defined, the diffraction system number is requested.

An overview of existing scans is displayed if you type "?" instead of the scan number. The first free number is chosen if you type RETURN instead of the number. If you enter an existing scan number then the contents will be displayed with the options: "Accept, Change, Delete = Change :=".

You will return to the Assemble menu without altering the scan if you type "A". If you choose "Change", then the questions are displayed with the existing answers as defaults.

You can describe the scan by the scan name of maximum 20 characters. Then you have to choose between Step scan, Continuous scan and Psi scan.

For a continuous scan you must enter speed and sample interval (degrees two theta). At speeds lower than 0.1 deg/s it is advised to choose step scan. The computer displays the measuring time per interval. The time per interval must be a multiple of .05 seconds. If it is not, then the system calculates the nearest speed that gives a correct time per interval. New speed, angle interval, and time are displayed.

Stepscans require a stepsize (degrees two theta) and sample time per step, from these, the theoretical speed is calculated (without time used for movements). Further dialogue is as for continuous scans.

After you have entered the starting and final angle of the scan, the system calculates and displays the total measuring time.

Psi scans are step scans with one extra parameter, the psi (theta-tilt) angle. The system displays $\sin^2$ (psi) after you enter psi. It is advisable to only use positive psi angles, together with one or more zero-psi scans. The maximum psi angle should be at least 10 degrees less than half of the starting angle of the scan (for example: if the starting angle is 140° the maximum psi angle is 60°). Refer to Chapter 11.6, Stress Analysis for more information.

7.2.5 PHASES

The measurement parameters of one diffraction peak are defined in a PHASE. The measurement results of ´Phases´ combined with a quantitative analysis program, are used for the calculation of the weight fractions (concentrations) or mass of the compounds that they represent and the result is stored in a QI file. The analysis program must be assembled separately (refer to Section 7.2.3) and the calibration constants have to be established in the Calibration program (refer to Section 7.5 in this Chapter). You will find a description of the principles of quantitative analysis and advice on the practical use of the programs in Chapter 11.3 of this manual.

You can enter the Assemble phases mode by giving "P" in the ASSEMBLE PARAMETER FILES mode. If there is more than one diffractometer, the system will then ask for which diffractometer the phase must be assembled.

Next the phase number has to be entered:

If you enter "?" the system will display a map of the phase numbers in use for this diffractometer.

If you just give RETURN, the system will assign the first (lowest) free number and start the assemble dialogue.

If you enter a free number, the system will start the assemble dialogue.

If you enter the number of an existing phase, the system will display the parameters of that phase and the question: "Accept, Change, Delete = Change :=". If you choose "Change" the assemble dialogue will be displayed with the ´old/existing´ parameter values as proposed values.

7.2.5.1 Assembling (of) a Phase

First enter a phase name of up to 20 characters, then choose one of: "Peak phase, Area phase = Peak phase:=". For a description of these two phase types refer to Chapter 11.3.3.

Peak Phase.

If you choose Peak phase, the system asks for the peak angle followed by the measuring time at that angle.

Then you can enter up to two background angles. If you enter 0 (zero) for the first background angle value the system will not ask for any more background angles, but will go on to the next stage (Search for maximum). If you enter any background angle values the system will ask for the next value, until you have entered two of them or given the value 0; at which time the system will request "Measuring time at background angle(s)= 1.00=".

Finally you can choose whether or not to search for the position of the peak maximum before the peak and background measurements are taken. (This is recommended for Peak phases). If the peak has shifted from the theoretical position, the background points will have been shifted a similar amount and will be compensated for if you give "Yes" to this request. If you choose "Yes", you must also enter the number of measuring points on both sides of the peak, the step size between the points and the measuring time at each point.

Area Phase.

If you choose Area phase, you have to define: the scan speed, the starting angle and the finishing angle. The system will then display the time required for this area scan.

Then you can enter up to two background angles. If you enter 0 for the first background angle value the system will not ask for any more background angles, but will go on to the next stage (Search for maximum). If you enter any background angle values the system will ask for the next value, until you have entered two of them or given the value 0; at which time the system will request "Measuring time at background angle (s) = 1.00:=".

Finally you can choose whether or not to search for the position of the peak maximum before the peak and background measurements are taken. If the peak has shifted from the theoretical position, the background points will have been shifted a similar amount and will be compensated for if you give "Yes" to this request. If you choose "Yes", you must also enter the number of measuring points on both sides of the peak, the step size between the points and the measuring time at each point.

NOTE: If you make (a) raw data file(s) of (a) representative sample(s), it is possible for you to find the angles for the peak and the backgrounds; and the starting and finishing angles for areas with the aid of the Graphics, Plot program; using the cursor and the P (position) command, as described in Chapter 10.

7.2.6 SYSTEM PARAMETERS

The computer uses the system parameter file for all general or basic parameters needed for the operation of the system as a whole. There are three kinds of system parameters, they are:

General system parameters

Terminal parameters

Diffractometer parameters

NOTE: Do not change (assemble) the System Parameter file during Data collection.

You can enter the Assemble System Parameters mode by giving "S" in the ASSEMBLE PARAMETER FILES mode.

7.2.6.1 General System Parameters

The general system parameters define:

- whether there is a system printer and plotter
- the connection and type of the plotter
- the storage device (disc and UFD) for the help files
- the default storage device (disc and UFD) for the reference data base.

A system printer or listing device will print messages from the system, for example the Data collection log file. Optionally data files for all users can be listed on the system printer.

On an RSX operating system the printer is controlled by the Queue Manager program. A queue is a waiting line, in this case a list of files or messages waiting to be sent to the printer. The system requests: "Printer available: Yes, No". The connection number for the system printer is defined during SETUP, refer to Chapters 3.2 and 5.3.

If a plotter is part of the system, you can choose a Parallel or Queued connection. The latter option sends all Plot tasks to the plotter via the Queue Manager. After the instruction to make a plot, the terminal is returned to the dialogue menu, you can do further work while your plot is being produced whenever the plotter is free for it. If the plotter is connected in "Parallel" to a terminal you can request plots from this terminal only, and the terminal is not free as long as the plotter is busy.

The system requests the plotter connection number and type of plotter. Refer to Chapter 5.4. After you enter the type of plotter the system asks how many pens that you will have on the plotter. If the plotter is PM8151 or PM8154 the system will then ask whether or not you want to use automatic paper transport. In Professional 350/380 systems you can enter whether or not you have a plotter, if you have a plotter the number of pens has then to be entered.

In an APD system (Chapter 3), by default, the help files are stored on DL0:[1,2], or DW1:[200,300] with a Professional 350/380 system. The default reference data base is the Inorganic PDF data base DL1:[300,57], or DW1:[300,57] with a Professional 350/380 system. You choose the Organic PDF data base by entering DL1:[300,56], or DW1:[300,56] with a Professional 350/380 system.

If you have Created and assembled your own User reference data base, then enter the device and UFD (probably [300,60], refer to Chapter 7.4).

```
ASSEMBLE PARAMETER FILES                                  17-JAN-86   9:48

BATCH FILE, ANALYSIS PROGRAMS,
GONIO SCANS, PHASES, SYSTEM PARAMETERS, LIST := S

General, Terminal, Diffractometer := G

Printer available?  Yes, No = Yes :=

Plotter: None, Parallel, Queued = Queued :

Plotter connection number =  5 :

Plotter type: Tektronix, PM8151, PM8154 = PM8151 :
Number of pens = 7 :
Automatic paper advance?  Yes, No = No :=

Initial ref data base directory = DU0:[300,57] :=
Help  and  error text directory = DU1:[300,102] :
```

Figure 7.1 Example of System Parameters, General

7.2.6.2 Terminal parameters

The system displays the connection number of the terminal from which you work and the characteristics of the terminals which already have been specified. The first time the system assumes that a video terminal is connected to connection number 0. With a Professional 350/380 system the SET UP button can be chosen.

The connection number, type, number of lines per screen and number of characters per line are displayed, and for graphics terminals the type number is also displayed.

If you request to assemble a terminal connection number which has already been defined, then the system displays the choice:

"Change, Delete = Change :=".

Then the Terminal type must be defined, options are:

"Printer, Video terminal, Graphics terminal".

If you define Printer, then the system requests:

"Line width (chars) = 80 :=".

If you define Video terminal, then the system requests:

"Number of lines = 24 := " and:

"Line width (chars) = 80 :=".

If you choose Graphics terminal, then you must define the type:

"HP 2648, 4010/4012, 4014, 4105, 4107, 4109, 4112, 4113, 4114, 4115, 4116 = :="

The default types Tektronix 4010 and 4012 have a fixed number of lines (35) and line width (74 characters). For the Tektronix type 4014, 4114, and 4116 graphics terminals you can choose any one of 4 different character sizes. The largest character is number 1 and the smallest is number 4. The latter offers the largest number of lines per screen and the largest number of characters per line. The default character size is number 2. For the type 4115 you can choose one of two character sizes 1 or 3, number 1 (the largest size) is default. If you type "?" instead of a number, the system will display the possible character sizes.

The Hewlett Packard graphics terminals 2648A and 2623A have a line width of 80 characters. They have an internal buffer memory that contains the alphanumeric data that disappears from the top of the screen if another line is added to a full screen. The APD system requests to define the: "Number of lines in internal buffer = 150 :=". The buffer of the HP 2648A can contain 150 lines (6 screens). The HP 2623A can store up to 48 lines of text (2 screens).

```
ASSEMBLE PARAMETER FILES                                    17-JAN-86   9:49

BATCH FILE, ANALYSIS PROGRAMS,
GONIO SCANS, PHASES, SYSTEM PARAMETERS, LIST := S

General, Terminal, Diffractometer := T


Specified terminals:

Connection    Type    Lines    Width    Graphics type
----------    ----    -----    -----    -------------
    0          VT       24       80
    1          PR               132
    2          GR      150       80     HP  2648
    3          GR       38       81     TEK 4014
    4          GR       32       80     TEK 4107

This is terminal connection:  1

Assemble terminal connection number := 3

Change, Delete = Change :=

Terminal type: Printer, Video terminal, Graphics terminal = Graphics terminal :=

Graphics terminal type: HP2648, 4010/4012, 4014, 4105,
4107, 4109, 4112, 4113, 4114, 4115, 4116 = 4014 :=

Charactersize: 1, 2, 3, 4 = 2 :=
```

Figure 7.2 Example of System Parameters, Terminal

7.2.6.3 Diffractometer parameters

In the Diffractometer parameters, each of the diffractometers can be defined. The diffractometer system numbers should be consecutive and start at 1.

Firstly you must enter the identification of the diffractometer system. You can use up to a maximum 60 characters to describe the diffractometer and/or the laboratory. Then a number of diffractometer parameters have to be entered. These parameters can be divided into three types:

A. Parameter values which will be stored only for future print out:

X-ray tube anode material	Default:	Cu
Tube focus type		Broad
Generator voltage and current		45kV, 60mA
Take-off angle		6 degrees
Receiving slit		0.2mm
Scatter slit		Fixed, 1 degree
Detector type		Proportional

B. Parameter values which will be used by the system for calculations or decisions:

Wavelength (K-alpha$_1$)	Default:	1.540598 *
Wavelength (K-alpha$_2$)		1.544390 *
Intensity ratio (alpha$_2$/alpha$_1$)		0.50000
Divergence slit		Automatic
Illumination length		12.5mm
Monochromator used		Yes
High angle limit of goniometer		140 degrees **

* The system contains different default values for wavelength, according to the anode material that you selected. These were extracted from the International Tables for X-ray Crystallography, Volume IV, citing: Bearden, J. A. Rev. Mod. Phys. 39, 78(1967). These values are:

Anode Material	K-alpha$_1$ Wavelength in Å	K-alpha$_2$ Wavelength in Å
Cu	1.540598	1.544390
Mo	0.709300	0.713590
Co	1.788965	1.792850
Fe	1.936042	1.939980
Cr	2.28970	2.293606
Other	1.540598	1.544390

You can list or change these values with the option "TABLES" in System Preparation (refer to Chapter 7.6).

** Carefully adjust and check the high angle limit switch on the goniometer. Be sure that the value entered in the Diffractometer parameters is smaller than the actual switch position. If something does go wrong and the goniometer is ´blocked´ at the high angle limit; press the RESET button on the PW1710 Diffractometer control and correct the high angle limit.

C. Parameter values which will be used by the computer for control of the diffractometer (for more detail refer to the PW1710 Operating Manual):

PHD lower and upper level	Default:	20%, 80%
Sample changer		None
Spinner available		No
- if yes: Sample spinning		Yes
Recorder		None
- if PM 8203A or PM 8210:		
Recorder on		No
Recorder speed		10mm/degree 2 theta
Time constant		S
Ratemeter full scale		5E3
PW1710 display: Left		Angle
Right		Counts

Several of these parameters can be changed temporarily during Data collection if a Batch file is used. For each Job in the Batch file you can choose different values for:

PW1710 display: Left	Default:	Angle
Right		Counts
PHD lower and upper level		20%, 80%
Recorder on? Yes, No		No
Ratemeter full scale		5E3
Ratemeter time constant		S
Recorder speed		10
Sample spinning? Yes, No		No

7.2.7 LIST

It is possible to show a listing of all assembled parameters on a Terminal or on the system Printer, or to write a listing on an ASCII file (a LIST FILE, extension .LIS) for later use.

A listing of batch file parameters can be given per job or per sample, or all parameters of a batch file can be given at once.

Analysis program parameters are listed per diffractometer system with options for displaying the following:

the map of analysis program numbers in use,

the parameters of a particular analysis program number,

the parameters of all analysis programs concerning scans only, quantitative analysis, or identification,

or all parameters of all analysis programs defined for this diffractometer system.

NOTE: For Identification analysis programs, only name and scan number are listed.

For gonio scans the options are: Map, Number, Continuous, Step, Psi scans, All.

For phases the options are: Map, Number, Peak phases, Area phases, All.

For the system parameters the options are: General, Terminal, Diffractometer, All.

7.3 SYSTEMATIC ERROR CORRECTION

7.3.1 INTRODUCTION

With the Systematic Error Correction routine the systematic errors inherent to the technique of x-ray diffraction can be described to the system by one of four functions. This enables you to compensate for the systematic errors at a later stage. It is also possible to evaluate and correct the differences between diffraction patterns (DI files) or DI files and PDF patterns (outliers can be eliminated). The four functions are:

Linear	-	b . [2 theta] + c
Quadratic	-	a . [2 theta] . [2 theta] + b . 2 theta + c
Sine	-	b . sin [2 theta] + c
Combined	-	a . sinsquare [2 theta] + b . sin [2 theta] + c
Best	-	All of the above models are executed, and by a least squares analysis the best curve is selected.

7.3.2 THE ERRORS

In principle, each diffractometer measurement contains systematic and random errors. Some of these are related to goniometer geometry, others are due to specimen and measuring conditions, and some can be caused by the ´packing´ of the d-spacings (rounding-off errors).

The largest systematic error for phase identification is specimen displacement, this error is also the easiest to correct. This error is corrected for automatically in the IDENTIFY (SANDMAN) program and the value is displayed.

All errors and their effect on the phase identification are discussed in ´Automated Powder Diffractometry´, Norelco Reporter/Vol.30 No. 1X, February, 1983, APD Special Issue, page 40.

7.3.3 APPLICATION

For routine diffractometry the error calibration function has only to be determined at installation, and thereafter, periodically checked. The standards normally used for calibration are: Si, alpha-quartz, or any phase that exhibits the characteristics of a good standard. The standard can be either an external standard sample or an internal standard material mixed with the ´unknown´ sample.

The error calibration routine can also be used as an analysis routine in special applications. For example: comparisons of diffractograms of phases or mixtures (visual recognition, PLOT). In that case the standard can be: one phase of the mixture, or the mixture, or a JCPDS PDF reference pattern, or a user reference pattern.

7.3.4 PRINCIPLE OF THE PROGRAM

First the theoretical d-spacings of a standard are requested, these d-spacings are converted to angles as soon as the program has checked the wavelength of the relevant diffraction system. Then the observed peaks in $^{o}2\theta$ are requested. The observed peaks can be read from a DI file or manually input ("manual").

The standard and observed peaks are stored in a disc file with the extension EC (default file name = SECFILE.EC).

The next step is to calculate a calibration function to describe the curve through the difference between observed and standard peak angle. The parameters are stored in the same file as the observed and standard reflections. The observed 2θ angles can be corrected using the selected error correction function. The contents of the file containing the standard can be edited; and the curve to be used for fitting, as well as the maximum acceptable difference can be made default.

7.3.5 SYSTEMATIC ERROR CORRECTION (COMMANDS)

The optional commands within the systematic errors program are:

NEW STANDARD — The error correction procedure commences by selecting a suitable standard to be used as a reference.

The standard can be a stable specimen of known composition, like for example: alpha-quartz, Si, or a reference pattern from the reference data base, or a pattern input by the operator.

OBSERVED PEAKS — The relevant DI file is selected and peaks are read in.

FIT CURVE — The difference between the observed and the theoretical angle is described by the Systematic Error Correction Function. This is done by fitting either: a linear, quadratic, sine, combined curve (quadratic sine) or best. If best is selected the best curve from all of the other possibilities is selected on the basis of the outcome of a least squares routine.

STORE SECF — The parameters of the curve are stored in an EC file. You can give it a name relating to the application that it corresponds to.

LIST — A listing of the EC file can be made and can be output to Terminal, Printer or File.

PLOT
EDIT
DEFAULTS/OPTIONS — The commands PLOT, EDIT and DEFAULTS/OPTIONS enable you to see the results and if necessary change the parameters of the systematic error correction function.

With the command EDIT it is possible to remove "outliers" from a curve that has been fitted. The remaining angles should then be re-fitted to provide a relevant curve.

CORRECT DI FILE — DI files can be corrected with the calculated systematic error correction function.

7.4 REFERENCE DATA BASE

7.4.1 INTRODUCTION

A reference data base is a collection of 16 disc files that contain all the information necessary for searching through the reference patterns, for matching those reference patterns with an experimental pattern, and for displaying the results. There are two types of data base, they are:

- PDF Data base, issued by JCPDS, specially packed by Philips for efficient use in the phase identification program (SANDMAN). In 1985 it contained 35,204 inorganic compounds and 20,615 organic compounds. It can also contain 1,534 user reference patterns (in set 0) in both the Inorganic and Organic data bases.
- User Reference Data Base. In a user data base, up to 9,999 user reference patterns (measured or typed-in) can be combined to a user-specific reference data base.

For maintenance of the reference data base(s), refer to Chapter 7.4.5.2.

The purpose of the Reference data base program is:

A. To add user patterns to an existing data base,
B. To create and fill a new data base, and
C. To assemble and list subfiles.

To perform one of the above actions, you must give "R" when you are in SYSTEM PREPARATION, this will then present to you the optional commands in the Reference Data Base menu.

7.4.1.1 OPTIONAL COMMANDS

The optional commands available within the Reference data base program are:

ASSEMBLE SUBFILE	General	(subfile name) + dialogue
	Reference patterns	(subfile name) + dialogue
	Frequency	(subfile name) (min. access count)
	Combine	dialogue
USER REFERENCE PATTERN	Assemble user pattern log file	+ dialogue
	Load user ref. patterns	
CREATE NEW DATA BASE (maximum number of patterns)		
HISTOGRAM		
LIST	Reference pattern	(ss-nnn)
	DI file	(file name)
	Sub file	(subfile name)
	User pattern log file	
OPTIONS/DEFAULTS	Representation	peak position (d-spacings or angles)
		peak intensity (counts or normalized)
	Listings	minerals (formula or names)
		header listing (none, short or full)
		data listing (none, short or full)
		listing to (terminal, printer or file)
	Data base	device and UFD

These commands are all described in paragraphs 7.4.2 to 7.4.7.

7.4.2 ASSEMBLE SUBFILE

A subfile is a collection of patterns that have a common property. Their main application is to restrict the search process in IDENTIFY (SANDMAN) to a specific part of the data base; but it is also possible to display the contents of a subfile on the terminal by means of the LIST Subfile command. If, for instance, you want to know which Cu-Ni compounds are in the data base, you can easily assemble one subfile that contains all Cu-patterns, another subfile with all the Ni-patterns, and make a logical "AND" combination file which can be listed to show all the desired Cu-Ni compounds.

A subfile is organized as a map of the data base with one bit for each pattern; a one means that the pattern belongs to the subfile, and a zero means that it does not. So, a subfile is tightly connected to the data base that it belongs to. When the sequence of userpatterns changes after a reload of patterns, the subfile has to be changed too. When the subfile is created for another (or 'old') data base it is also necessary to change the subfile.

7.4.2.1 Assemble subfile, General

This command is used to assemble a subfile based on general pattern characteristics. The file name will have the extension SF. When the subfile name refers to an existing SF file, the contents will be shown on the terminal, with the possibility to change or delete the file. If you type "?" instead of a subfile name, then a directory of all subfiles in your UFD is displayed.

Patterns can be selected on five different characteristics: Minimum quality, PDF subfiles, Lattice types, Elements present and Elements absent.

The subfile with the name "RESTRICT.SF" can also be defined in "ANALYSIS, IDENTIFY" (refer to Chapter 11.2).

7.4.2.1.1 Minimum quality

Six quality data marks from high to low quality: Star, Calculated, Indexed, Blank data (no mark), Questionable data (marked on card with a circle) and "No restrictions" (all patterns, "deleted" included). If one of those grades is chosen, only patterns with data marks equal to or better than the one chosen are included in the subfile. A quality grade is selected by typing the first letter.

7.4.2.1.2 PDF subfiles

Seven PDF subfiles can be chosen: Organics, Inorganics, Minerals, Nonminerals, FEPS, NBS patterns, and Alloys. System requests if you want to choose one or more PDF subfiles with: "PDF subfiles? Yes, No = No :=".

The logical "AND" function is used when more than one subfile is selected. For example when FEPS and Minerals are selected, the subfile will contain patterns that are minerals and are also present in the FEPS file. (The minerals in the FEPS file).

7.4.2.1.3 Lattice types

The lattice type has to be given with the crystallographic symbol (refer to command USER REFERENCE PATTERN Assemble log file). The logical "OR" function is used when more than one lattice type is selected. If you enter "?" the system displays the table of codes.

7.4.2.1.4 Elements or groups known to be present

This information cannot be defined in the subfile RESTRICT.

Input can be: (upper and lower case letters are accepted)

A. Any element name from H (1) to Bk (97)

B. One of the following functional groups:
H2O OH NH2 NH3 NH4 CN NO2 NO3 PO3 PO4 P2O7 CO3 SO4 IO3 BO3 SeO3 SeO4 AsO4 CrO4 MoO4 VO4 UO2 ClO4 WO4 BeF4 SiO4 ReO4

C. LAN for all lanthanides: La (57) - Lu (71)
ACT for all actinides: U (92) - Bk (97)

D. A range of elements indicated by - (for example: "H - FE" or " H - Fe" or "h - fe").

If you enter "?" the system will display these input possibilities.

NOTE: D, Cf and Es are not accepted in a subfile; however they do occur in some reference patterns. If you want to include or exclude the patterns with these elements you should use a subfile type Ref patterns (refer to Section 7.4.2.2). Pattern numbers can be found in the Alphabetical Index (JCPDS).

The logical "OR" function is used when more than one element or group is selected. For instance, if Cu and Ni are selected to be present, the subfile includes all patterns that contain Cu or Ni or both.

7.4.2.1.5 Elements or groups known to be absent

Input is the same as for elements present. But in case of more than one element or group, the logical "AND" function is used to combine them. For instance, when Fe and Zn are selected to be absent, the subfile includes only the patterns that contain neither Fe nor Zn.

If you enter "?" the system will display these input possibilities.

7.4.2.1.6 Combination of pattern characteristics

When two or more of the above five pattern characteristics are combined, the logical "AND" function is used. For instance:

Quality: Calculated
Subfile: Minerals
Elements present: Cu, Ni

Patterns in this subfile must have quality marks "Calculated" or better and must be in the Minerals-file and must contain Cu or Ni.

NOTE: "Elements present" are deleted from the list of "elements absent" before the subfile is prepared by the system.

7.4.2.2 Assemble subfile, Ref patterns

With this command, a subfile can be made up consisting of specific reference patterns. The patterns have to be typed with their reference (PDF) set number and number in that set (ss-nnn).

7.4.2.3 Assemble subfile, Frequency

Command to make a subfile based on a minimum value of the access counter (refer to paragraph 7.4.6 "Histogram"), the maximum value is 32 767. In this way you can build your own Frequently Encountered Phases subfile.

7.4.2.4 Assemble subfile, Combine

This command can be used to combine subfiles. Up to four input files can be specified and the logical operator can be And, Or, Exclude, None. This is explained in figures 7.3 and 7.4. Shaded areas represent reference patterns contained in the combined subfile.

A and B are subfiles with different characteristics of the reference patterns.

In this example 1, 2 and 3 are subfiles in which Fe, S and O respectively are defined as present. Subfile 4 is based on the pattern number of Si (internal standard material, reference number 27-1402).

7.4.2.5 Subfile Maintenance

Each time an addition, deletion or change has been made to the Data base (with the User pattern, Load command) or if a new data base version is used, all sub files must be changed. For general and combined subfiles this can be done with the command "Change to current data base". For subfiles based on frequency and reference pattern number this is not possible. Therefore it is advisable to make hard copies of your subfiles of the latter type, so that in future you can make new ones by typing the pattern numbers. For a new version of the data base (PDF) frequency cannot be used, in which case you could also use the pattern numbers.

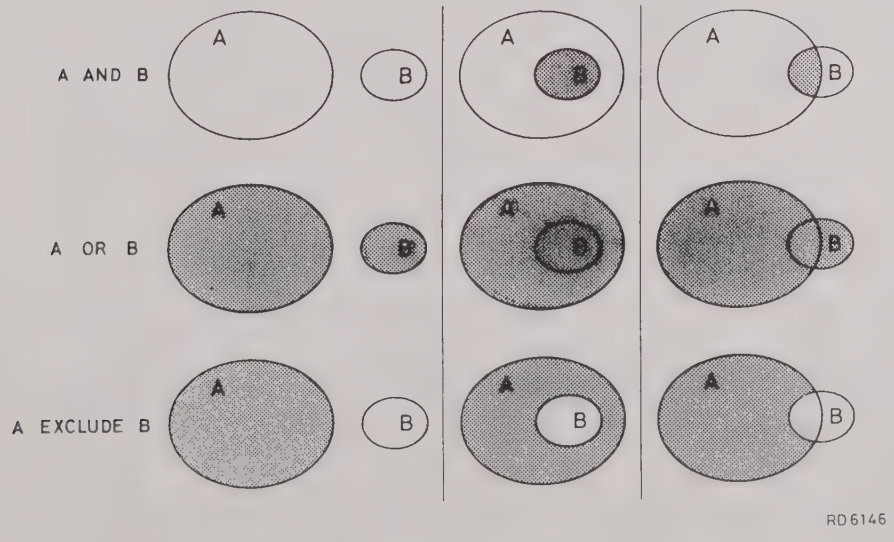

Figure 7.3 The Logical Operations And, Or and Exclude

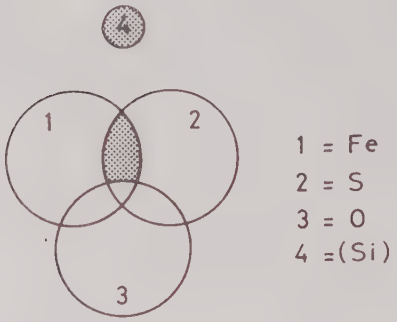

Figure 7.4 The Logical Operations And, Or and Exclude in Combination

7.4.3 USER REFERENCE PATTERNS

You use this command when you wish to make a change to an existing data base, to add a new reference pattern, or to delete a reference pattern. You must give "U" in the REFERENCE DATA BASE mode to get into User Pattern.

In order to save space, user patterns are stored in sequence directly after each other. It is not possible to change one loaded pattern without affecting the others. So, if a loaded pattern is changed or deleted, all patterns have to be reloaded, which can take a considerable amount of time (several minutes to a quarter of an hour or more, depending on the size of the data base and the number of user patterns).

Access to a data base is always via a log file. A log file contains a list of the DI file names of the user patterns in the data base, and a note of where in the data base the user pattern is located. Two steps are required to put a user pattern into the data base (or take one out). First the list of file names in the log file is edited by the subcommand Assemble user pattern log file, and then the actual loading is performed by the subcommand Load, which takes the files listed in the log file, and loads them into the data base.

Each reference data base can have a log file (PDF Inorganic and Organic, and User reference data bases).

7.4.3.1 User Reference Patterns, Assemble user pattern log file

The program displays the maximum number of patterns (in a User Reference data base) and the highest loaded pattern number as a warning for the operator. The necessary information is written to the log file by means of a dialogue. Most questions have a default answer; only the DI file name must explicitly be given by the user.

User reference pattern number (equivalent to PDF number).
After you have given an existing pattern number the program requests: Accept, Change, Delete.

If you choose "Delete" the user pattern is deleted from the log file. Following patterns keep their own number.

When a pattern which already has been loaded to the data base is deleted, then all the patterns from the log file will be reloaded at the next Load command, thus deleting the pattern from the data base.

If you want to delete all user patterns you should delete the pattern with the highest number first, the system then prompts the next highest pattern number automatically.

User patterns are stored in set zero, so that the pattern can always be retrieved with number 0-n (or even n). The program gives the first available number, but you can overwrite it if you want.

DI file name. The user reference pattern can be the result of the Peak search sub-program, or entered manually by the EDIT Alpha$_1$ PEAKS command in the IDENTIFY (SANDMAN) or PATTERN TREATMENT programs.

Quality datamark, possible answers are:

S	"Star" quality
C	Calculated data
I	Indexed data
B	Blank, no datamark (default)
Q	Questionable data (marked with a circle)
D	Deleted pattern

Subfile. JCPDS PDF subfile mark, possible answers are:

I	Inorganic, non-mineral (default)
O	Organic, non-mineral
D	Dual (Inorganic/organic) non-mineral
MI	Inorganic, mineral
MO	Organic, mineral
X	Cross indexed mineral
A	Alloy

"?" displays this table.

NOTE: User patterns are always included in the FEP-file.

Lattice type designation, possible answers are:

C	primitive cubic	O	primitive orthorhombic
F	face-centered cubic	P	body-centered orthorhombic
B	body-centered cubic	Q	base-centered orthorhombic
T	primitive tetragonal	S	face-centered orthorhombic
U	centered tetragonal	M	primitive monoclinic
R	rhombohedral	N	centered monoclinic
H	hexagonal	Z	triclinic

"?" displays this table. There is no default.

Number of atoms per unit cell, must be a value between 0 and 255. The number may be fractional with one decimal, in which case the range is between 0.0 and 25.5.

Formula. Input in a free case or exact, depending on setting under Options/ defaults (refer to Section 12.2.2.1). All element names from H (1) to Es (99) are recognized. D is not accepted, Cf and Es are but cannot be included in subfiles or in chemistry input.

Mineral name; maximum is 35 characters.

The command can be terminated by typing a slash (/) at the question about the user reference pattern number.

7.4.3.2 User Reference Patterns, Load user reference patterns

With this command, the actual loading into the data base is executed. If, since the last loading, the only action was to add user patterns, the new patterns are loaded into the data base. If patterns that have already been loaded into the data base have been changed or deleted, then all the user patterns are removed from the data base and the whole log file is reloaded.

A reload increments the version number of the data base. The version number does not change when patterns are only added to the data base.

The user pattern log file contains the DI file names of the user patterns, but not the diffraction lines as they are contained in the DI file of each pattern.

The command Load uses the log file as well as the DI files. They must be contained on the disc, each time the log file has to be loaded.

The log file is automatically stored in the UFD of the reference data base. For the DI files it is advisable to store them in a special UFD (copied from your ´normal´ work UFD).

7.4.3.2.1 Creating a Special UFD

The ´special´ UFD must be created, using the RSX command: "CREATE/DIRECTORY" (refer to the Software Instruction Manual Chapter 4.3). It is advisable to create the ´special´ UFD(s) on the device where the Data base is stored, except for MICRO/PDP with Winchester drive and floppy diskettes (refer to Section 7.4.5.1). With Professional 350/380 you have to choose "Create Directory" in the "Disk/diskette services" menu (refer to Section 7.4.5.1).

For an easily surveyable file organization it is advisable to choose UFD [300,157] for the patterns that have to be added to the Inorganic file [300,57]. Accordingly you could create UFD [300,156] for the patterns additional to the Organic file [300,56]. If you have a user reference data base [300,60] you could choose UFD [300,160] for the DI files belonging to it. We suggest that the ´Special´ UFD for DI files in systems with floppy disc drives (RSX and P/OS)is prepared on a diskette (refer to Sections 7.4.5.1.2 and 7.4.5.1.3).

Make it a habit to first copy a DI file from your ´normal´ UFD to the ´special´ one. For the User pattern Add command specify the DI files from the ´special´ UFD. In this way it is certain that the DI files can be found for the next load command.

NOTE: If you choose almost the same DI file names for the user reference patterns (for example: REF01.DI and so on), then copying and further file handling is made much easier (COPY REF.DI in this case).*

If a Back-up of the data base (on RL02 disc) is made, the copy will automatically contain the latest set of DI files. Further it is easier to add the user patterns to a next updated version of the PDF data base.

7.4.4 CREATE NEW DATA BASE

Command to create a new data base. The maximum number of patterns has to be given. The program responds with the number of disc blocks (256 words each) required for this data base.

The maximum number of patterns cannot be extended later, therefore it is advisable to define a more than sufficient number. Moreover, after the first pattern, a further increase in the number of patterns only slightly increases the number of blocks required, this is shown in the following list:

Maximum number of patterns	Required number of disc blocks
1	167
10	169
100	202
200	239
300	275
400	314
500	349
1 000	535
2 000	908

If you give the command "User reference patterns, Assemble log file" (SYSTEM PREPARATION, REFERENCE DATABASE, refer to Chapter 7.4.3.1), the system will display "Maximum number of user ref patterns" and "User ref pattern number last loaded".

An error message is printed when device and UFD refer to an existing data base. After successful creation of the data base files, the new data base is automatically opened.

NOTE: Before you can create a reference data base, the device and UFD that should contain the data base must have been created. (refer to Chapter 7.4.3.2.1)

7.4.5 DATA BASE

At the first start up of the program, the data base of the APD1700 system parameter file is taken.

The year, the device and UFD, the version number and the number of user patterns are shown on the terminal. You can use the Options/defaults, Data base command to change to another data base.

7.4.5.1 Disc Preparation for User Reference Data Base

7.4.5.1.1 For RSX Systems with RL02 Disc Drive

If you want to build and use a User Reference data base for phase identification, you must make the following preparations:

- Exit from APD and Log out
- Type "LOG SYSTEM/SYSTEM"

If you want to use an empty disc (or one that can be overwritten) in DL1 it must be, 'inserted, tested, initialized and mounted' (mounted means: 'software connected'). Do that as follows:

- $RUN $BAD
  BAD>DL1:
  BAD>CTRL/Z
  $ALLOCATE DL1:
  $INITIALIZE DL1: volume label ('volume label' is the name that you wish to give the disc in a maximum of 12 alpha-numeric characters).
  $DEALLOCATE DL1:
  $@LBO:[1,2] MNT DL1

Now you must make a place for the data base on the disc, you do this by creating a directory, for example: [300,60] corresponding with the directories for the PDF data base.

- $CREATE/DIR DL1:[300,60]

In the same way, prepare a directory for the DI files which are the input for the user patterns:

- $CREATE/DIR DL1:[300,160]

Log out and log in to your own UFD, start APD, select Reference data base, and build up your new data base. Refer to paragraphs 7.4.3 and 7.4.5.

7.4.5.1.2 For RSX Systems with Winchester and Floppy (RX50K) Disc Drives

It is practical to have all of your DI files of user reference patterns on floppy diskettes as then they cannot be accidentally deleted or changed and they do not take up space on your work disc (the Winchester).

NOTE: This can be used for a maximum of two diskettes per data base (one in DU1 and one in DU2), that is a maximum of about 300 user patterns.

Prepare a diskette as follows:

- Exit from APD and Log out
- Enter the system as a priviliged user: "LOG SYSTEM/SYSTEM"
- Insert a diskette in DU1 and then test and initialize it:

  $RUN $BAD
  BAD> DU1:
  BAD> CTRL/Z
  $ALLOCATE DU1:
  $INITIALIZE DU1: Volume label ('volume label' is the name that you wish to give the disc in a maximum of 12 alpha-numeric characters).
  $DEALLOCATE DU1:
  $MOUNT/PUBLIC DU1: Volume label

- Create a directory for your user pattern DI files, most practically the same as your 'work' directory (for example: 300,1):

  $CREATE/DIR DU1:[300,1]

- Log out and then Log into your own UFD.
- Copy the DI files from your 'work' directory onto the new diskette:

$COPY DUO:'Filename1'.DI DU1: and 'Filename2' and so on until you have given all the file names (or use COPY REF*.DI DU1:, refer to Section 7.4.3.2.1)

and then Load User patterns (from the diskette), Exit and:

- Log out of your own UFD and then Log in as a privileged user.

```
$LO
$LOG SYSTEM/SYSTEM
$DISMOUNT/PUBLIC DU1:
```

- Remove the diskette from DU1 and store it until the next time that you have to load user patterns.

7.4.5.1.3 For P/OS Systems with Winchester and Floppy (RX50K) Disc Drives

It is practical to have all of your DI files of user reference patterns on floppy diskettes as then they cannot be accidentally deleted or changed and they do not take up space on your work disc (the Winchester).

NOTE: This can be used for a maximum of two diskettes per data base (one in DZ1 and one in DZ2), that is a maximum of about 300 user patterns.

Prepare a diskette as follows:

- Exit from APD
- Insert a diskette in DZ1 and initialize it (using disc services menu)
- Create a numbered directory using the command language (the command language option must be installed on the Professional 350/380 personal computers), we advise you to use the same directory on the floppy diskette as your 'work' directory (200,200).

  $CRE/DIR DZ1:[200,200], it must be a directory in the 200 group.

- Copy the DI files from your 'work' directory to the new diskette:

  $SET DEFAULT [200,200]
  $COPY DW1:'Filename1'.DI DZ1: and 'Filename2' and so on until you have given all the file names (or use COPY REF*.DI DZ1:, refer to Section 7.4.3.2.1)

- Start APD and Load Userpatterns (from the diskette)
- Remove the diskette from DZ1 and store it until the next time that you have to load user patterns.

7.4.5.2 Maintenance of the Reference Data Base

7.4.5.2.1 For RSX Systems with RL02 Disc Drive

Upon receipt of a new data base disc, and before using it, you should make a back-up copy. Use the indirect command file BACKUP and store the original disc in a safe place when finished.

If you regularly add user patterns to, or delete patterns from, the data base, it is advisable that you make back-up copies regularly. This is also advisable if you want to make use of the Histogram and Frequency subfile commands in the program Reference data base. The method is described in the Software Instruction Manual Chapter 6.

The user pattern log file only contains the DI file names, not the diffraction lines which are contained in the DI files. This implies that those DI files must be kept for loading on your next version of the PDF data base.

It is advisable that you create (RSX-command) a special UFD on the device (for example: disc DL1:) that contains the PDF data base. For storage of DI files of user patterns to be added to the Inorganic file you could create and use for example [300,157]. This number resembles strongly that of the Inorganic file itself, [300,57]. In the same way you could use [300,156] for patterns to be added to the Organic file, which is in UFD [300,56]. If you have a user reference data base in UFD [300,60], then you could keep the DI files in [300,160].

To copy the user patterns added to an existing PDF data base to a new PDF data base version:

- Create the required UFDs on your work disc (DL0): [300,57], [300,56], [300,157] and so on as necessary.
- Now copy the user pattern log file(s) and all relevant DI files from DL1 to the system disc (DL0:). Choose Utilities, Copy and from:

  DL1:[300,57]UPLOG.PDF for the Inorganic file and/or:
  DL1:[300,56]UPLOG.PDF for the Organic file.

  To: DL0: brings the log file(s) on the system disc.

  Then from:
  DL1:[300,157]*.* and/or DL1:[300,156]*.*,
  to: DL0: copies all necessary DI files to the system disc.

  If subfiles of the type 'Frequency' exist, it is advisable to list them (Short data = all pattern numbers) at this stage.

Now you can dismount the 'old' PDF-disc (DL1) and insert and mount the new PDF data base disc. For the commands to dismount and mount refer to the Software Instruction Manual Chapter 4.3.

- Create the 'special' UFD on the new data base disc in DL1.
- then copy the user pattern log file(s) and all relevant DI files from the system disc to the new DL1.
  from: DL0:[300,57]UPLOG.PDF and/or DL0:[300,56]UPLOG.PDF
  to : DL1: , and
  from: DL0:[300,157]*.* and/or DL0:[300,156]*.*
  to : DL1: brings all relevant data to the new disc.

Before you can use it, first choose SYSTEM PREPARATION, Reference data base, Userpattern, and Load. Then each line of the user pattern DI files is inserted in the correct place in the new PDF data base.

When you have checked the above procedure (for example, by listing some of the user reference patterns) you can delete DL0:[300,57]*.*, [300,56] and [300,157] to make space on your work disc.

NOTE 1: If you are going to use a new version of the PDF data base, or if you have used the Userpattern Load command, the subfile(s) for Restrictions must be assembled again (refer to Section 7.4.2.5).

NOTE 2: Subfiles based on Frequency cannot now be used, refer to Chapter 7.4.6.

7.4.5.2.2 For RSX Systems with Winchester and Floppy (RX50K) Disc Drives

It is advisable to do the following actions for one data base at a time, this Section describes the procedure for the inorganic data base [300,57].

- Insert the ´Userpattern diskette´ (refer to 7.4.5.1.2) into DU1 and copy the userpattern log file to it:

```
$LOG APD/APD
$MOUNT DU1: volume label
$COPY [300,57]UPLOG.PDF DU1:[300,1]
```

If subfiles of the type ´Frequency´ exist, it is advisable to list them (Short data = all pattern numbers) at this stage.

- Delete all the data base files:

```
$DEL [300,57]*.PDF;*
$DISMOUNT DU1:
```

- Remove the Userpattern diskette and load the new data base (refer to the Software Instruction Manual Chapter 7.6.3.5)

- Insert the Userpattern diskette and copy the User pattern log file to the new data base.

```
$MOUNT DU1: volume label
$COPY DU1:[300,1]UPLOG.PDF DU0:[300,57]
```

- Log off as a priviliged user and then log into your own UFD, start APD and Load Userpatterns (from the diskette) and then Exit.

```
$DISMOUNT DU1:
```

- Remove the Userpattern diskette from DU1 and store it until the next time that you have to load user patterns.

7.4.5.2.3 For P/OS Systems with Winchester and Floppy (RX50K) Disc Drives

It is advisable to do the following actions for one data base at a time, this Section describes the procedure for the inorganic data base [300,57].

- Insert the ´Userpattern diskette´ (refer to 7.4.5.1.3) and copy the userpattern log file to it:

```
$COPY [300,57]UPLOG.PDF DZ1:[200,200]
```

If subfiles of the type ´Frequency´ exist, it is advisable to list them (Short data = all pattern numbers) at this stage.

- Delete all the data base files:

```
$DEL [300,57]*.PDF;*
```

- Remove the Userpattern diskette and load the new data base (refer to the Software Instruction Manual Chapter 9)

- Insert the Userpattern diskette and copy the User pattern log file to the new data base.

```
$COPY DZ1:[200,200]UPLOG.PDF DW1:[300,57]
```

- Start APD and Load Userpatterns (from the diskette).

- Remove the Userpattern diskette from DZ1 and store it until the next time that you have to load user patterns.

7.4.6 HISTOGRAM

All patterns in the data base have an access counter. The counter is incremented each time the pattern is positively identified in the IDENTIFY (SANDMAN) program, and each time it is addressed in the COMPARE program and in the LIST commands (refer to paragraph 7.4.8 and Chapter 12).

The command HISTOGRAM gives an overview to the terminal, printer or file of the number of patterns that have been accessed at least one time. The histogram shows for 15 ranges of the access-counter: the number of patterns within each range, and the total number of patterns above that range. From this, you can determine a minimum access count for the Assemble subfile, Frequency command.

In a new data base (next year's PDF data base) all access counters are zero. You could use Assemble subfile, Ref patterns to transport your Frequency knowledge. List the subfile based on frequency when the "old" data base is mounted (short data). Make a new subfile after the "new" data base has been mounted, typing all the pattern numbers from the listing.

7.4.7 LIST

A command to show Reference patterns, DI files, Subfiles and the User pattern logfile on the terminal or the printer, or to write these data in an ASCII file.

A subfile can contain many (even all) patterns of a data base. Displaying these pattern data can take a very long time. If you choose a short data presentation (numbers only Options/defaults, Listings) the system will ask if you want all information or the header only (if the subfile contains more than 500 patterns). If you choose a full data presentation the question is asked if the subfile contains more than 100 patterns. Listings to the printer can be skipped by entering "/" (without RETURN).

If you type "?" (without RETURN) the system displays the status of the preparation of the print file (APD.DMP).

7.4.8 OPTIONS/DEFAULTS

You may change the following groups under Options/defaults:

- Representation of:
  - * Peak positions: D spacings or angles (2θ). This affects the commands LIST, Reference pattern and DI file.
  - * Peak intensity: Counts or normalized (largest peak in DI file equals 100). This affects the commands LIST and DI file.
  - * Minerals: Formula or name. Input and output can be as chemical formula or mineral name (if applicable). This affects the commands LIST, Reference pattern and the output in ANALYSIS, Identify (Sandman).
  - * Formula input: Exact or free case. An example of exact input is CaCO3 where free input format could be: CA C O3 or ca c o3. Output is always in exact format. This affects the command User reference patterns.

- Listings, the following options:
  * Header listing: None, Short, Full or Optional. Short header affects LIST, DI file. Optional means that you have to choose at the time you give the LIST command.
  * Data listing: None, Short, Full or Optional. This affects LIST, DI file and Subfile.
  * Listing to: Terminal, Printer or File.
- Data base: The data base that you want to use can be specified by entering device and UFD. This affects the Reference data base program and the Identify program (Sandman).

7.5 CALIBRATION

7.5.1 INTRODUCTION

Before quantitative analysis can be performed the calibration constants for the analytical phases have to be established. Calibration constant is the name for the proportionality constant used for converting net intensity into weight fraction or concentration.

Calibration constants are calculated from known weight fractions and net intensities of calibration standard samples. The weight fractions are entered via the keyboard (Assemble Calibration Set), the net intensities are entered from data files (Input QI Files). The net intensities are calculated from the gross counts measured at the calibration standard samples. Before such measurements can be done you have to assemble phases and analysis programs (refer to Chapters 7.2.5 and 7.2.3 respectively). If applicable, the overlap factors and/or constant background corrections have to be established ´off-line´ before you start the quantitative analysis (refer to Chapter 11.3.3).

Four types of calibration constant can be distinguished, depending on the calculation model defined in the analysis program:

- Absolute calibration constants, used in an analysis program with the General model.
- Straight line calibration constants used with the Straight line model.
- Relative calibration constants used with the Matrix flushing, Binary and Internal standard models.
- Mass calibration constants used with the Thin sample model.

The analysis program used during the calibration procedure may differ from the one used for data collection.

You may use from 1 to 25 calibration standard samples to calibrate your system for the phases contained in an analysis program. If you use more than one standard sample, then linear regression analysis will be applied by the system to establish the calibration constants. In this way you can reduce the influences of:
- counting statistical errors
- ´weighing´ errors (precision of input concentrations)
- inhomogeneity of the samples
- non-random orientation of the grains in the samples.

For a detailed description of the principles and methods of quantitative analysis, refer to Chapter 11.3

7.5.2 ASSEMBLE CALIBRATION SET

In a calibration set for a number (maximum 25) of calibration standard samples, the information on calculation model to be used and phase numbers (by means of input of the analysis program number to be applied) is combined with the input on the weight fractions (concentrations) or masses of the phases in the respective standard samples.

The system commences by requesting the diffractometer system number (if more than one diffractometer is used) and the analysis program number to be applied. If you enter "?" instead of an analysis program number, the system will display a 'map' of the existing analysis programs for the diffractometer. The calculation model used in the defined analysis program is displayed by the system together with the number of standard samples previously specified in the calibration set. Refer to figure 7.5.

Then you may enter the sample number for which the concentrations have to be entered. The sample identification is entered next, it can be used for checking whether you try to combine the correct intensities with the concentrations by comparing it with the sample identification of the QI file (Input QI files).

```
CALIBRATION QUANTITATIVE ANALYSIS                          23-JAN-86  15:23
-------------------------------------------------------------------------

ASSEMBLE CALIBRATION SET, INPUT QI FILES, CALIBRATE,
PLOT, EDIT CONSTANTS, MONITOR, LIST, OPTIONS/DEFAULTS := A

Diffractometer system number = 1 :=

Analysis program number := 3

Model: Straight line

 0 samples specified in calibration set

Sample number =  1 :=

New sample

Sample identification =                          := MIXTURE 28 20 52

Phase number =   1 :=

Concentration (%) =   0.00 := 28
New total of analytes (%):  28.00

Net intensity :=

Phase number =   2 :=

Concentration (%) =   0.00 := 20
New total of analytes (%):  48.00

Net intensity :=

Phase number =   3 :

Concentration (%) =   0.00 := 52
New total of analytes (%): 100.00

Net intensity :=

Phase number :=

Total of analytes (%): 100.00
```

Figure 7.5 Assemble Calibration Set

Then you are requested to enter the phase number, default is the first phase number in the analysis program for the first request. The following defaults are the same as the next phase numbers of the analysis program until the last phase number has been specified. If you change an existing calibration set, the phase numbers already specified are presented as defaults. If you enter "?" instead of a number the system will display the phase numbers applicable to the analysis program and (in the case you change an existing calibration set) further data on the phases.

Next you may enter the concentration (weight fraction) or mass of the phase you have chosen. You also may enter the net intensity (and measuring precision) for the phase. You may skip this input if you intend to enter the intensities with the "Input QI Files" command.

NOTE: Phase calibration for use in Thin sample analysis programs should be done with infinitely thick samples, because of loss of accuracy during thin sample conversion.

Then the input for the next phase is requested, and so on until you have input the data for the last phase of this sample. You may delete a phase in an existing calibration set. If you give RETURN instead of a number, the total of the concentrations of the analytical phases in this sample is displayed, and the next sample number is requested.

You may delete the last sample from an existing calibration set by entering "0" (zero) after its number has been proposed, and then "Delete".

7.5.3 INPUT QI FILES

The input of the net intensities of the respective phases in (a) calibration standard sample(s) may be done with this command.

The system requests diffractometer system number (if more than one diffractometer is defined) and analysis program number. This is used for combining the intensities with the appropriate calibration set, for calculation of the net intensities and for application of the correct calculation model.

If you enter "?" instead of an analysis program number, the system will display a ´map´ of the existing analysis programs for this diffractometer. Then you have to enter the number of the sample of the calibration set for which you want to enter the intensities. The system will display how many phases are specified for this sample in the calibration set. Refer to figure 7.6.

You have to enter the quantitative data file name (QI file). The analysis program number used for collecting the data in this file does not have to be the same as the analysis program of the calibration set. The system displays a listing of data from:

- the QI file:
  - sample identification (of the measured sample)
  - diffractometer system number
  - gross intensities of the phases measured
  - background intensities
  - background corrected intensities

- the analysis program of the calibration set:
  - sample information like MAC, total of analytes, and so on
  - overlap corrections and net intensities of the phases in the analysis program
- the calibration set:
  - sample identification (in the calibration set)
  - concentrations, net intensities, precision, and date of measurement

Future changes (improvements) of the calibration constants can be made by measuring a new (group of) calibration standard sample(s) and then entering their intensities with "Input QI files".

```
CALIBRATION QUANTITATIVE ANALYSIS                          23-JAN-86  15:34

ASSEMBLE CALIBRATION SET, INPUT QI FILES, CALIBRATE,
PLOT, EDIT CONSTANTS, MONITOR, LIST, OPTIONS/DEFAULTS := I

Diffractometer system number = 1 :=

Analysis program number := 3

Model: Straight line

Sample number =  1 :=

 3 phases specified

Quantitative data file name = PRTS05J02.QI :=


Quantitative data file: PRTS05J02.QI     8-FEB-85  23:57
Sample  identification:
Diffractometer  system: 1

Phase   Phase  Phase    Gross      Background  Background  Corrected  Prec
number  type   angle  intensity   intensity   correction  intensity   (%)
------  -----  -----  ---------   ---------   ----------  ---------  ----
   1    Peak   28.470    9044.0       121.0       121.0     8923.0    1.2
   2    Peak   27.450    3271.8       127.7       127.7     3144.2    2.2
   3    Peak   35.170     625.0       141.6       141.6      483.4    7.6

Analysis program   3: QUANT 3 PHASES STR L  Model: Straight line

Phase    Overlapping     Net     Prec
number   phase  corr  intensity  (%)
------   -----  ----  ---------  ----
   1              0.0    8923.0   1.2
   2              0.0    3144.2   2.2
   3              0.0     483.4   7.6

QI file monitor intensity  :       0.0  Prec (%):  0.0
Calibration mon intensity  :   36235.6
Monitor ratio              :   1.00000  Prec (%):  0.0

Sample  1: MIXTURE 28 20 52

Phase    Conc        Net        Prec     Measurement     Phase
 no       (%)     intensity     (%)    date       time  name
------   -----    ---------    -----   ---------  -----  -----
   1     28.00       8923.0      1.2   8-FEB-85  23:57  SILICON
   2     20.00       3144.2      2.2   8-FEB-85  23:57  TI O2
   3     52.00        483.4      7.6   8-FEB-85  23:57  AL2 O3
```

Figure 7.6 Input QI files

7.5.4 CALIBRATE

With this command the actual calculation of the calibration constants is done using the concentrations from the calibration set and the net intensities derived from the QI file(s). Refer to figure 7.7.

The system requests the diffractometer system number (if more than one diffractometer is defined) and analysis program number. If you enter "?" instead of the analysis program number the system will display a ´map´ of the existing analysis programs for this diffractometer.

The system will display the calculation model specified in the analysis program, the phase numbers of the analytical phases, and data concerning the way the absorption is treated (depending on the model used).

For the matrix flushing and binary models (relative calibration constants) the system requests which phase should be the calibration reference (that is the phase used for the calculation of the relative errors in the calibration constants) and which phase is to be the storage reference phase (that is the phase with the relative calibration constant equal to 1.00). For these requests you are advised to choose the default answers by entering RETURN.

Then you must choose whether to calibrate all the phases in the analysis program applicable to this calibration set, or single phases one by one. If you choose single phases, then you must enter the phase number. The system displays the information on all samples in the calibration set for this phase, together with its calibration constant and the precision. This enables you to check the result, especially whether the precision is what you expect.

If you are satisfied with the results you may store the calibration constant. Alternatively you can plot the ´calibration curve´ of the phase, on the graphics terminal or on the plotter if it is part of your system. The data can be listed again as described before, on the printer or on the terminal, depending on the choice in Options/defaults. If you are not satisfied with the calibration results, you can, for example: eliminate a sample in the calibration set if it seems to be an ´outlier´ and calibrate again, or you can temporarily exclude one or more samples from the set.

NOTE: If you choose to calibrate all the phases at once, then it is not possible to check the calibration results before storing them. In this case all calibration constants are stored directly after they have been calculated.

7.5.5 PLOT

You may plot ´calibration curves´ on your graphics terminal or your plotter. First you have to define the diffractometer system number and the analysis program, then you may choose which phase has to be plotted. Refer to figure 7.8.

For relative calibration constants (models: matrix flushing and binary) it is possible to choose another phase as the calibration reference phase in order to check the results (the result is not and cannot be stored).

```
CALIBRATION QUANTITATIVE ANALYSIS                          23-JAN-86  15:51

ASSEMBLE CALIBRATION SET, INPUT QI FILES, CALIBRATE,
PLOT, EDIT CONSTANTS, MONITOR, LIST, OPTIONS/DEFAULTS := C

Diffractometer system number = 1 :=

Analysis program number := 4

Model: General

Analytical phases:

  1  2  3

Calibration model: General, Straight line, Relative = General :=

Exclude samples?  Yes, No = No :=

Calibrate: Single phase, All = Single phase :=

Phase number =   1 :=
```

Sample number	MAC * Net intensity	Precision (%)	Concentration (%)	Calculated (%)	Difference (%)
1	535112.9	1.2	28.00	27.90	0.35
2	441628.7	1.6	22.00	23.03	-4.67 D
3	951363.4	1.0	50.00	49.60	0.79

```
Phase   1: SILICON
Calculated general calibr constant: 0.5214E-06  Prec (%): 0.74

Plot, List, Store constant = Store constant :=
```

Figure 7.7 The Calibrate Command

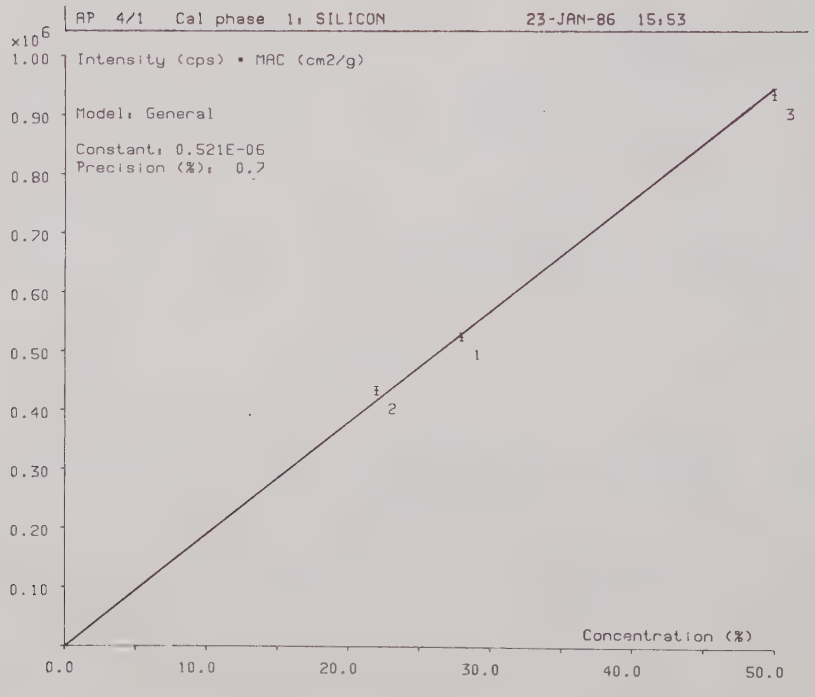

Figure 7.8 Plot of a Calibration Curve

7.5.6 EDIT CONSTANTS

This command can be used to manually change calibration constants.

You must enter the diffractometer system number (if more than one diffractometer is used) and what type of calibration constant you want to change: General, Straight line, Mass, or Relative. For the latter type of constant the next question is: which is the phase number of the calibration reference, you may enter a phase number different from the one used during the previous calibration.

Then the phase number of the analytical phase of which you want to edit the constants has to be entered. The system requests whether you want to accept, change or delete.

7.5.7 MONITOR

You can restore the current monitor value if the most recent monitor measurement was incorrect, you can introduce a new version of the monitor if the old one gets damaged, you can edit monitor values and you can list them.

NOTE 1: Do not use any Monitor commands while measuring the monitor sample as it could cause the new monitor values to be incorrectly stored.

NOTE 2: If it is not strictly necessary, do not use any Monitor commands except List. Unlike most other commands in APD1700, these commands should not be used for 'learning-in' purposes or 'trying-out'.

7.5.7.1 Restore Current Monitor

If something was (or went) wrong during the measurement of the monitor sample (wrong sample or generator setting), an incorrect intensity will be stored as the current monitor value Mc. The way to achieve the correct situation is either to measure the sample again using the correct settings, or to use the command "Restore current". The latter option is explained with the following examples:

In figure 7.9A the situation just before an incorrect measurement is illustrated with the output of the "List, Current monitor" and the "List, Replacements" commands.

Subsequently a measurement was done using incorrect settings (in this example a narrower receiving slit of 0.2mm), the result of the measurement is shown in figure 7.9B

If you give the command "Restore current" the system asks you to enter the name of the last QI file with a correct monitor value Mf in the header. In most cases this is the QI file of the monitor: in this example it is "MONIT2.QI" as shown in figure 7.9C:

The situation is then restored as shown in figure 7.9D:

```
CALIBRATION QUANTITATIVE ANALYSIS                          5-DEC-85  15:46
-------------------------------------------------------------------------

ASSEMBLE CALIBRATION SET, INPUT QI FILES, CALIBRATE,
PLOT, EDIT CONSTANTS, MONITOR, LIST, OPTIONS/DEFAULTS := M

Monitor: Restore current, New version, Edit, List := L

List: Current monitor, Replacements = Current monitor :=

Listing to: Terminal, Printer, File = Terminal :=

 Diffr    Monitor    Precision      Measurement       Monitor
system  intensity        (%)       date       time   version
-------------------------------------------------------------
  1      55182.7         0.0      5-DEC-85  15:32       1
  2          0.0         0.0                            1
  3          0.0         0.0                            1
  4          0.0         0.0                            1

List: Current monitor, Replacements = Current monitor := R

Listing to: Terminal, Printer, File = Terminal :=

Diffr     Monitor    Replacement    Replacement
system    version       ratio          date
-------------------------------------------------
  1           1                      None
  2           1                      None
  3           1                      None
  4           1                      None

List: Current monitor, Replacements = Current monitor := /
```

Figure 7.9A Restoring of Current Monitor (A)

```
List: Current monitor, Replacements = Current monitor :=

 Diffr    Monitor    Precision      Measurement       Monitor
system  intensity        (%)       date       time   version
-------------------------------------------------------------
  1      40453.3         0.0      5-DEC-85  15:50       1
  2          0.0         0.0                            1
  3          0.0         0.0                            1
  4          0.0         0.0                            1

List: Current monitor, Replacements = Current monitor := R

Diffr     Monitor    Replacement    Replacement
system    version       ratio          date
-------------------------------------------------
  1           1                      None
  2           1                      None
  3           1                      None
  4           1                      None
```

Figure 7.9B Restoring of Current Monitor (B)

```
ASSEMBLE CALIBRATION SET, INPUT QI FILES, CALIBRATE,
PLOT, EDIT CONSTANTS, MONITOR, LIST, OPTIONS/DEFAULTS := M

Monitor: Restore current, New version, Edit, List := R

Last monitor/QI file name = MONIT2.QI :=


Quantitative data file: MONIT2.QI     5-DEC-85  15:50
Sample  identification: MONITOR RS 0.2 MM
Diffractometer  system: 1

QI file monitor intensity:   55182.7  Prec (%):   0.0   5-DEC-85  15:32
Current monitor intensity:   40453.3  Prec (%):   0.0   5-DEC-85  15:50

QI file monitor will be restored as current monitor
Are you sure?  Yes, No = No := Y

Monitor: Restore current, New version, Edit, List := L

List: Current monitor, Replacements = Current monitor :=
```

Figure 7.9C Restoring of Current Monitor (C)

```
 Diffr    Monitor    Precision      Measurement      Monitor
system  intensity        (%)      date       time   version
------------------------------------------------------------
  1      55182.7         0.0     5-DEC-85  15:32       1
  2          0.0         0.0                           1
  3          0.0         0.0                           1
  4          0.0         0.0                           1

List: Current monitor, Replacements = Current monitor := R


Diffr     Monitor    Replacement    Replacement
system    version        ratio          date
-----------------------------------------------
  1           1                      None
  2           1                      None
  3           1                      None
  4           1                      None

List: Current monitor, Replacements = Current monitor := /
```

Figure 7.9D Restoring of Current Monitor (D)

7.5.7.2 New Version

If the original external monitor sample has been damaged, you do not have to start a complete new calibration procedure for all General, Straight line and Mass constants that are used in analysis programs in which a monitor ratio has been specified; instead, you can measure another sample - the new monitor - as shown in figure 7.10A. For simplicity in this example the same measurement is used as in the previous section "Restore Current Monitor".

This measurement should be done as soon as possible after you discover that the previous monitor has been damaged. You can then be confident that the current monitor value is still valid.

```
QUANTITATIVE ANALYSIS                                          5-DEC-85  16:03
-------------------------------------------------------------------------------

CALCULATE, LIST, OPTIONS/DEFAULTS = CALCULATE :=

Quantitative data file name = MONIT2.QI :=


Quantitative data file: MONIT2.QI     5-DEC-85  15:50
Sample  identification: MONITOR RS 0.2 MM
Diffractometer  system: 1

Analysis program number =  99 :=

Phase   Phase  Phase    Gross     Background  Background  Corrected  Prec
number  type   angle  intensity  intensity   correction  intensity   (%)
-------------------------------------------------------------------------
  99    Peak  26.650   40453.3       0.0         0.0      40453.3    0.0

Analysis program  99: MONITOR (ARK STONE)   Model: External monitor

Current monitor intensity:     55182.7  Prec (%):  0.0   5-DEC-85  15:32

Phase  99 stored as current monitor
```

Figure 7.10A Replacing the Monitor (A)

The situation is then as shown in figure 7.10B, the second monitor appears to give a lower intensity.

NOTE: The new monitor sample can be a totally different material, measured with another analysis program (another phase).

```
List: Current monitor, Replacements = Current monitor :=

 Diffr   Monitor   Precision     Measurement      Monitor
system  intensity     (%)      date       time   version
-------------------------------------------------------
  1     40453.3       0.0     5-DEC-85  15:50       1
  2         0.0       0.0                           1
  3         0.0       0.0                           1
  4         0.0       0.0                           1

List: Current monitor, Replacements = Current monitor := R


Diffr    Monitor   Replacement   Replacement
system   version      ratio         date
-----------------------------------------
  1         1                     None
  2         1                     None
  3         1                     None
  4         1                     None

List: Current monitor, Replacements = Current monitor := /
```

Figure 7.10B Replacing the Monitor (B)

When you give the command "New version", the system asks for the file name of the new monitor. Then the system displays the QI file monitor intensity Mf (last value of the ´old monitor´) and the current monitor intensity Mc (the ´new monitor´) for the same diffractometer system as the QI file was measured on. The ratio of the two intensities "New/old monitor replacement ratio" is displayed with the options: "Accept, Change, Remeasure new monitor".

Choosing "Accept" automatically gives you the new monitor version number (in this case 2); this will then be the effective number if you confirm that you are sure it is the correct new monitor version.

```
Monitor: Restore current, New version, Edit, List := N

New monitor QI file name = MONIT2.QI :=


Quantitative data file: MONIT2.QI     5-DEC-85  15:50
Sample  identification: MONITOR RS 0.2 MM
Diffractometer  system: 1

QI file monitor intensity:   55182.7  Prec (%):   0.0   5-DEC-85  15:32
Current monitor intensity:   40453.3  Prec (%):   0.0   5-DEC-85  15:50

New/old monitor replacement ratio:   0.73308  Prec (%):   0.1

Accept, Change, Remeasure new monitor = Change := A

New monitor version number will be  2
Are you sure?  Yes, No = No := Y
```

Figure 7.10C Replacing the Monitor (C)

```
Monitor: Restore current, New version, Edit, List := L

List: Current monitor, Replacements = Current monitor :=

 Diffr   Monitor    Precision      Measurement      Monitor
system  intensity      (%)       date       time    version
------------------------------------------------------------
  1      40453.3        0.0      5-DEC-85  15:50       2
  2          0.0        0.0                             1
  3          0.0        0.0                             1
  4          0.0        0.0                             1

List: Current monitor, Replacements = Current monitor := R

Diffr    Monitor    Replacement    Replacement
system   version       ratio          date
-----------------------------------------------
  1          2         0.73308       5-DEC-85
  2          1                        None
  3          1                        None
  4          1                        None
```

Figure 7.10D Replacing the Monitor (D)

The List current monitor and list replacements show the new situation.

The phase (calibration) monitor intensity Mp of the corresponding diffractometer has been multiplied with the monitor replacement ratio; this is all the "Recalibration" that has to be done. If applicable this must be repeated for all the diffractometers of the system.

NOTE: In 'old' QI files (files that do not have the most recent Monitor version) the monitor intensity Mf is multiplied with the monitor replacement ratio at the moment that they are used for calculation or calibration. This means that old QI files also give correct results after "New version" has been given.

7.5.7.3 Edit Monitor Values

This command allows you to edit monitor values (in case for example: something had gone wrong using the previous command). You can edit the current monitor, the phase calibration monitor, or a QI file monitor.

For the first two options you have to enter the diffractometer system number for which you want to edit (a) monitor value(s). The existing monitor value is displayed together with the options: accept, change, set to current monitor. With the change option you can change the monitor intensity, its precision, and the measurement date and time.

The "Edit QI file monitor", "Set to current monitor" option can be used for instance after the "Restore" command if a number of QI files have been measured following a wrong monitor measurement. Note that the QI file headers then contain an incorrect monitor intensity.

7.5.7.4 List

Current monitor values and replacement ratios can be Listed as shown in figure 7.10. The same parameters can be listed in ANALYSIS, Quantify.

7.5.8 LIST

You can list calibration sets, calibration data of phases, and calibration constants. The listings are sent to the printer, displayed on your terminal or written on an ASCII file depending on your choice in Options/defaults.

First you have to define for which diffractometer system you want to have the data listed. Further dialogue depends on the type of data you want to have listed.

Calibration Set

You have to enter the diffractometer system number and the analysis program number for which the calibration set was designed. Then you can choose whether the data for all samples or a single sample be listed.

The following will be listed for the defined sample(s):

- for all the phases: The concentration with net intensity, or mass with mass related intensity precision and date and time of the measurement of the calibration standard sample.
- for the sample: The sample information such as the total of analytes, or total mass.

Phases

You have to enter the diffractometer system number and the analysis program number for which you want the phase(s) to be listed. For analysis programs that refer to relative calibration constants (matrix flushing, binary, internal standard) the system displays which is the reference phase. For matrix flushing and binary programs you may choose another phase as reference. Then you must define whether you want the data for one single phase to be listed, or for all phases.

The output shows:

- For each sample in the calibration set:
  - sample number
  - net intensity (straight line calibration constants) or: MAC x net intensity (general calibration constants) or relative intensity (relative calibration constants) or mass related intensity (mass calibration constants).
  - precision (as percentage of intensity)
  - concentration, for straight line and general calibration constants, or: relative concentration (concentration of analytical phase divided by concentration of reference or standard phase) for relative calibration constants

- . calculated concentration: for each calibration standard sample the concentration is calculated as if it was an unknown sample
- . the difference between the actual and the calculated concentration (as percentage of the first). If only one standard sample has been used then the difference equals zero.
- . mass, calculated mass and difference between actual and calculated mass if a thin sample (mass calculation) calibration is performed.

- For the whole calibration set, for the required phase:
  - . calculated calibration constant
  - . precision (as percentage of the calibration constant).

Calibration Constants

Firstly you have to enter the diffractometer system number for which the calibration constants have to be listed. Then you may choose General, Straight line, Mass or Relative calibration constants to be listed.

If you choose General or Straight line calibration constants, then you must choose to list the calibration constant(s) for a single phase, for the phases defined in one analysis program, or for all (general or straight line) phases.

The output shows per phase:

- . phase number
- . calibration constant
- . precision (percentage of calibration constant)
- . calibration date and time
- . monitor intensity valid during measurement of the calibration standard sample
- . precision of the monitor intensity (as percentage)
- . measurement date and time of the external monitor sample of which the intensity is valid during measurement of the calibration standard samples.

For Mass calibration constants you may choose to list the calibration constants for a single phase or for all (mass) phases.

The output shows per phase:

- . phase number
- . calibration constant
- . precision (as percentage of calibration constant)
- . date and time of calibration of the phase
- . phase name

For Relative calibration constants you may choose to list the calibration constants for a single phase, for a group of phases with the same storage reference phase, for the phases defined in one analysis program, or for all phases with relative calibration contants, or to list the quotient of 2 relative calibration constants together with the precision calculated in the same way as for the calculation of concentrations.

The output shows per phase:

- . phase number
- . relative calibration constant
- . reference phase for which the calibration constants were stored
- . precision of the quotient of the calibration constants of this phase and of its precision reference phase (percentage of calibration constant)
- . precision reference (phase which was used as reference during calibration)
- . date and time of calibration of the phase

7.5.9 OPTIONS/DEFAULTS

The following default options can be chosen with the use of this command.

Listings

You may choose to have no output at all (only disc files will be written), short output, or full output during (automatic) analysis. Listings may be displayed on the printer or your terminal.

Representation

Concentrations can be represented in input and output as percentages or as (weight) fractions. Mass is always expressed in milligrams (mg).

7.6 TABLES

Two sets of tables can be referred to during System Preparation, the wavelengths and the Mass Absorption Coefficients. The tables can be edited and/or listed to check the constants which apply for the type of x-ray tube (anode material) which you define.

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8.1 INTRODUCTION

To collect data, you must give "D" when you are in the "MAIN MENU", this will then allow you access to the optional commands in the Data Collection mode. It is not possible to use the Data Collection mode with a VAX system.

8.1.1 OPTIONAL COMMANDS

The optional commands available within the Data collection program are:

EXECUTE

REPORT

DISPLAY/PLOT

PRIORITY SAMPLE

INTERPOSE SAMPLE

HALT

The commands: Display/Plot, Priority, Interpose, and Halt can only be given from the same terminal from which the measurement was started for the required diffractometer.

8.2 THE EXECUTE COMMAND

After the EXECUTE command the system requests the diffractometer system number, if more than one diffractometer is defined.

The system requests the name of the batch file that has to be executed. If you enter "?" instead of a name, a directory of the batch files in your UFD is displayed.

NOTE: Do not start Data Collection if anybody is changing (assembling) the System Parameters.

You give RETURN instead of a batch file name if you want to analyse a single sample according to one analysis program. The system requests the identification of the sample. The name of the Raw data file in which the measured data will be stored is requested. The system suggests the first six alpha-numeric characters of the identification. If there is additional sample specific information required for the execution of this analysis program, it will be requested at this time.

In order to start analysis, you must press RETURN when the sample or sample changer magazine are loaded.

NOTE: If you do not have a sample changer, the display will revert to the data collection menu for a short time before displaying the message asking you to give RETURN to start the analysis. During this short time, you must WAIT for the message before proceeding.

8.3 THE REPORT COMMAND

A Report gives the status of all active diffractometer systems. An example of a Report follows:

```
EXECUTE, REPORT, DISPLAY/PLOT,
PRIORITY SAMPLE, INTERPOSE SAMPLE, HALT := R

Diffr                    Meas  Work    Job  AnPr  1st  Current Current  Max
system   UFD      TT     type  file     no    no  sample sample  angle  counts
------------------------------------------------------------------------------
 1    [300, 1]  1    N  SILICO    1     8                      28.6   17556.
```

Figure 8.1 Example of a Report

The report shown in figure 8.1 tells you the following information:

Diffr system	1	Number of the diffractometer which is collecting data.
UFD	[300,1]	The directory to which the collected data is written.
TT	1	Terminal number from which the data collection was started.
Meas type	N	Measurement type. In this case Normal, can also be Priority, or Interposed sample.
Work file	SILICO	Name of the workfile.
Job no	1	The job number: starting at 1.
AnPr no	8	Number of the analysis program used to collect the data.
1st sample		Sample position of the first sample in this job. A blank space indicates that no batch file is used.
Current sample		The number of the sample currently being measured. A blank space indicates that no batch file is used.
Current angle	28.6	Current angle: the angular position of the goniometer at the moment the report was requested.
Max counts	17556.	The maximum number of counts per data point encountered up to the moment the report was requested.

8.4 THE DISPLAY/PLOT COMMAND

It is possible to display the results obtained so far on the sample being measured on video terminals or teletypewriters. Plotting of these results is done if the same command (DISPLAY) is given from a graphics terminal.

8.5 PRIORITY SAMPLE COMMAND

If you give the PRIORITY sample command, the system will halt the current measurement from a batch on the diffractometer of your choice. If a sample changer is in use, the sample being analysed will be returned to its magazine position. If the changer is fitted, but is not being used, the priority facility is not available.

You can place the high priority sample: either in the measuring position, or in the single sample position if you have a PW1775 changer.

Sample identification, raw data file name, and analysis program number are requested. The instrument starts when you give RETURN.

When the priority sample measurement is complete, the sample is returned (in the case of a PW1775 changer).

The system will then request: "Priority, Continue = Continue :=" . If you type "P", you can load another sample and repeat the priority procedure, or continue (RETURN) lets the system restart the interrupted measurement on the sample from the batch.

8.6 INTERPOSE COMMAND

If you have a PW1775 sample changer, you can INTERPOSE a sample when the measurement on the current sample is completed. You must place the sample to be measured 'in between' in the single sample position and enter the sample identification, raw data file name, and analysis program number. After the measurement of the interposed sample the system continues with the next sample from the magazine. The INTERPOSE command cannot be used when a priority sample is being measured on.

8.7 THE HALT COMMAND

HALT will interrupt the measurement on the diffractometer that you define. Then you can either continue the measurement, or stop it completely. In the latter case the Raw data file is closed if the analysis program is Scans only or Identify, a partial quantitative data file (QI) will be deleted. The sample is returned if a sample changer is used.

If you give the HALT command while the last sample is still being returned to the sample changer magazine, the system will display the message "Cannot halt diffractometer in current state".

When you stop a priority sample measurement, the system asks: "Resume joblist, Priority sample = Resume joblist := ". When you choose "Resume joblist" the system continues with the first sample to be measured. When you choose "Priority sample" the system asks for the new sample identification, raw data file name and analysis program number after which the measurement of the new priority sample is started.

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9.1 INTRODUCTION

The Pattern treatment programs are a set of programs to prepare measured data for identification, crystallographic analysis, and for graphical display.

Diffraction patterns, raw data, or intermediate results can be treated (sometimes MUST be treated) with different processes before further evaluation or a final analysis is made.

Peak search for crystalline diffraction lines or for maxima of 'amorphous' materials, correction of systematic diffractometer errors, elimination of the K-alpha$_2$ component in the raw data file, and data smoothing are the possibilities. A further possibility with this program is that you can input or edit a DI file via a keyboard.

In the APD1700 peak search routine, peaks are detected from the second-derivative of the measured diffractogram. During peak search the following files are used or can be generated:

RD	Raw data file.	(input)
DI	Detected peaks file.	(created)
BK	Background data file.	(created)
SM	Smoothed data file	(created optionally)
2D	Second derivative file.	(created optionally)

All these files except the DI file can be plotted in the GRAPHICS, PLOT program, the DI file can be displayed by activating MARK PEAKS in the PLOT program, or in COMPARE and ADD/SUBTRACT.

You can choose another file type as input file (same file name) by entering ".SM" or ".A2" and so on, for the file name. The default file type can be chosen in OPTIONS/DEFAULTS.

The creation of a smoothed data file or a second derivative file depends on default values which can be set (OPTIONS/DEFAULTS). If the PEAK SEARCH command is repeated and you choose not to overwrite the previous DI file, then another file with higher version number is made. All files can be called separately by their version number.

Before peak searching, the minimum and maximum value of the expected peak tip widths (width of the second derivative function on the zero line) can be requested optionally. Definition of a restricted width range might increase peak search selectivity and decrease run time. The DI file obtained from Peak Search can be automatically printed; this can be set in OPTIONS/DEFAULTS.

9.2 OPTIONAL COMMANDS

The optional commands within the Pattern treatment programs are as follows:

PEAK SEARCH — Locate the crystalline peaks and generate the background and DI file, and optionally a smoothed data and/or a second derivative file.

AMORPHOUS — Locate the amorphous peaks using the background file.

SYST ERROR CORR — Systematic error correction, refer to Chapter 7.3.

EDIT ALPHA1 PEAKS — New DI files can be input via the keyboard, or existing DI files can be changed or reduced.

K-ALPHA2 STRIP — Strip the K-alpha$_2$ component from the raw data file using the method of Ladell c.s. (J. Appl. Cryst. (1975) 8, p. 499) and generate the A2 file.

BACKGROUND REMOVAL — Creates a separated peaks (PK) file containing net intensities (raw data minus background).

DATA SMOOTH — Smoothing of a data file to provide an SM file in order to make a 'nicer' graphical display, and if required, be treated by pattern treatment routines.

LIST DI FILE — List the DI file on a terminal, printer or file.

OPTIONS/ DEFAULTS — Change or reset default values for crystalline as well as amorphous peaks. There are five groups of default values, they are:

1. The peak detection parameters (Peak search).
2. The option for the creation of a smoothed data and/or a second derivative file (Files).
3. The option for the assignment of beta peaks (Assignments). 'Other' peaks will be assigned (for example: interference spikes) unless you define to assign Alpha 1 to them.
4. The parameter for stripping of K-alpha$_2$ peaks from the raw data (K-alpha$_2$ strip). The number of weights and levers, which are used in deconvolving the alpha$_2$ profile, can be chosen. The weights weigh the K-alpha$_1$ distribution, and the levers represent the distance from the K-alpha$_1$ wavelength at which the corresponding weights have to be applied.
5. The parameters for making a listing of the DI file. There are parameters for the header, the data and the output device.

If the diffraction pattern has many overlapping peaks, and especially if those peaks are fairly broad, then it can be of advantage to strip the K-alpha$_2$ component from the raw data before searching for peaks. Sometimes small phantom peaks are created at the position where the K-alpha$_2$ was, because of increased background noise. With the exception of this disadvantage (phantom peaks), the results of a peak search after stripping K-alpha$_2$ are often better, as the sharper K-alpha$_1$ peaks show a better resolution, and therefore more separate peaks might be detected. The minimum significance of peaks to be detected is automatically increased when searching an A2 file.

For sensitive peak detection, both on background and on the sides of overlapping peaks, small angle intervals (step sizes) are recommended during data collection. At the same time, the reliability (precision and detection limits) of peak search results is improved by using a lower scan speed (longer measuring time per step). For example: a good result for complicated mixtures can be obtained using a step size 0.01° 2θ, measuring time per step 2 seconds.

The command PEAK SEARCH should be executed before the command AMORPHOUS, as during Peak Search the background file BK in which the amorphous maxima will be searched for is produced.

DATA SMOOTH can be requested in order to make ´nicer´ and more ´surveyable´ graphs in the PLOT and COMPARE programs (GRAPHICS, refer to Chapter 10). The system requests the raw data (or any other scan) file name, and the smoothing factor to be applied (1 - 5). The resulting minimum tip width will be displayed. In a subsequent Peak Search on such a smoothed file, peaks with a peak width smaller than the displayed minimum tip width will not be found.

The results of peak search can be listed as a table on a terminal or printer by invoking the LIST DI FILE command.

9.2.1 PEAK SEARCH ROUTINE

The Peak Search routine works in the following sequence:

1. Calculation of smoothed data and second derivatives from the raw data file applying up to five different smoothing factors.
2. Search for areas representing a peak.
3. Allocation of 2θ values to these areas.
4. Calculation of additional peak parameters.

9.2.1.1 The Calculation of Smoothed Data and Second Derivatives

The multipass peak search routine calculates smoothed data and second derivatives from the raw data file in up to five passes which are distinguished by the application of different smoothing factors. The number of passes depends on the step size (as used in data collection) and on the peak width range (as defined by minimum and maximum peak tip width). For calculating the smoothed data and the second derivatives a filter of the Savitsky Golay type is used (Anal. Chem Vol 26 No.8 July 1964 plus corrections).

Each pass produces data from which only a limited set of peaks can be detected. Peak tip widths in such a set will range from (approximately):

$$Wpmin = 3 \cdot SS \cdot 2^{L} \text{ up to } Wpmax = 2\ Wpmin$$

Wpmin = minimum peak tip width
Wpmax = maximum peak tip width

With L denoting the smoothing factor (or pass or loop number) and SS denoting the step size.

9.2.1.2 Detection of Diffraction Peaks

Possible diffraction peaks will be located in regions where the second derivative is negative. To accept such a region as a result of a diffraction peak, certain criteria have to be met.

From the smoothed data and the second derivatives the significance (S) of the peak under consideration is determined. This significance is in fact a measure of its probability of not being just a noise-induced peak.

Peaks having a significance higher than 1.0 are considered as being significant. Peaks having a significance lower than 0.5 are considered as being unreliable. A peak will be assigned as a diffraction peak if its significance is higher than a threshold value (the minimum significance of peaks to be detected Smin) which can be set up by the OPTIONS/DEFAULTS command.

The value of Smin determines the number of noise induced peaks (Nnpe) one can expect to be detected as crystalline peaks in a raw data data scan.

$$Nnpe = 2 \times \frac{\text{angle range}}{\text{Step size}} \times 0.0001^{Smin}$$

As an example this number is given for different values of Smin for a scan with a step size 0.02 degrees ranging from 10 to 110 degrees 2θ (5 000 data point) in the following table:

Minimum Peak Significance (Smin)	Expected number of noise induced (phantom) peaks (Nnpe) detected
0.25	100
0.50	10
0.75	1
1.00	0

9.2.1.3 Allocation of 2θ Value

The 2θ value of the accepted peak is determined by the top of a three point parabola fit through the smoothed data points. Alternatively, the centroid of the negative second derivative region can be chosen, or the minimum of a three point parabola fit through the second derivative data points.

9.2.1.4 Calculation of Additional Peak Parameters

During peak search several parameter values are displayed for each detected peak. These parameters are: sequence number, peak angle, tip width and number of counts. The smoothing factor applied and the peak significance can be optionally displayed.

The peak tip width is the width of the negative second derivative region, that means: the angular difference between the points of inflexion in the corresponding smoothed data points.

The number of counts is the value of the smoothed data at peak position.

The smoothing factor applied is equal to the number of the pass in which the peak was detected.

The peak significance was described in Section 9.2.1.2.

9.2.2 MODIFYING THE RESULTS OF A PEAK SEARCH

If you are not satisfied with the list of peaks detected by the Peak Search program, the results can be modified in three ways:

1. Add, delete or replace peaks manually from the DI file using the commands A(dd), D(elete), and R(eplace) in the cursor mode of the GRAPHICS, PLOT program. Refer to Chapter 10.2.1.

2. Add, delete or replace peaks manually via the keyboard using the EDIT ALPHA1 PEAKS command. Refer to Chapter 9.3.

3. Do the peak search again after having changed with OPTIONS/DEFAULTS one or more of the default values.

   Decreasing the minimum significance of peaks to be detected (Smin) will usually result in an increase of the number of peaks found. However, if Smin gets too low (lower than 0.5) an unacceptable amount of noise-induced 'phantom' peaks might be detected.

   For very quick scans, the value Smin = 0.6 is recommended, for slower scans, the value Smin = 0.75 might give better results. After resetting the defaults: Smin = 0.75.

   Knowledge about the tip widths of the peaks to be detected can be used to increase the reliability of the peak search results. An increase of the minimum tip width of peaks to be detected (Wpmin) might result in a decrease in the number of noise-induced peaks and in higher significances (corresponding to a higher smoothing factor) of the peaks detected.

   A decrease of the maximum tip width of peaks to be detected (Wpmax) might also result in a decrease in the number of noise-induced peaks. Both restrictions of the tip width range might decrease run time. After resetting the defaults are: Wpmin = 0.0 and Wpmax = 2.0 (full range).

9.3 EDITING OF A DI FILE

EDIT ALPHA1 PEAKS. By means of this command an existing DI file can be modified or a new DI file can be entered manually via the keyboard.

NOTE: If an existing DI file is the result of peak search (at a non-A2 file), then, after reading the file, the system will correct it by removing the K-alpha$_2$ peaks and shifting each K-alpha (1 + 2) peak and decreasing its intensity. Refer also to Chapter 13.2.3.

The dialogue for this command is:

"Peak positions representation: D spacings, Angles = D spacings :="
"Peak intensity representation: Counts, Normalized = Counts :="

For keyboard input and for display, the system requests the peak positions and the peak intensities representation.

"Create new pattern? Yes, No = No :="

When the answer is "Yes" a new DI file will be created, and when the answer is "No", an existing DI file can be modified.

If you chose "Yes" then you have to answer the following questions:

"Tube type: Cu, Mo, Co, Fe, Cr, Other = Cu =:"

Necessary for the system to select the correct wavelength (new patterns only). If you choose "Other" the system asks for the alpha$_1$ wavelength.

"Alpha 1 wavelength = 1.54060:="

"Sample identification = =:"

Maximum of twenty characters.

"Divergence slit: Automatic, Fixed=Automatic:="

When you choose "Automatic" the system asks for the illuminated specimen length in mm.

"Specimen length (mm) = 12.5:="

When you choose "Fixed" the system asks the aperture of the slit.

"Divergence (deg): 1/30, 1/12, 1/6, 1/4, 1/2, 1, 2, 4 = 1: ="

Next the specimen displacement will be asked for

"Specimen displacement (microns) = 0 :="

Known specimen displacement error in micrometers.
Number will be rounded to nearest multiple of 15.
Range is -600 to +600, default is 0.

"Minimum angle scanned = 1.000 :=" or "Maximum D spacing scanned = 88.2710:="
"Maximum angle scanned = 160.000 :=" or "Maximum D spacing scanned = 0.7822:="

Scan limits in D values or in degrees 2 theta, depending on the setting of the peak positions representation.

"Peak parameters to edit: All, Position/Intensity = All :="

"All" means that you can change any or all from: Position, Intensity, Width and Significance.

"Alpha$_1$ peak angle :=" or "D spacing :="

The system expects Alpha$_1$ peak angles or D spacings, depending on the setting of the peak positions representation.

If you chose for the peak intensity representation "Normalized" you have to give the Alpha peak angle/D-spacing of the 100 % peak first, because all other peak intensities are related to the 100% peak.

If you decided to edit an existing DI file by choosing "Create new pattern := No", the following questions have to be answered:

"DI file name = default :="

The system displays the number of Alphal peaks if the DI file contains Alphal and Alpha2 peaks (only Alphal peaks will be stored).

"Reduce, Edit peaks, Header, Divergence, List, Store :="

Reduce	Peaks can be categorically deleted, using as criteria for the peak parameters: Position, Intensity, Width, Quality.
Edit $alpha_1$ peaks	Individual peaks can be edited for the same peak parameters as above.
Header	Allows the following to be changed: Sample identification Specimen displacement Minimum and maximum angle/D spacing scanned
Divergence slit	Allows the following to be selected: Automatic or Fixed slit Specimen length (if automatic), the standard automatic divergence slit irradiates 12,5 mm of the sample.
List	Provides the resulting DI file.
Store	Enables the edited DI file to be written to the disc with an operator selected name. *NOTE: Only Alphal peaks will be stored.*

When you give RETURN the system asks for a file name to store the resulting DI file in.

When an existing DI-file is modified and you choose to remove the old version, all MS files with the same file name will also be deleted.

Typing a slash "/" causes you to exit from the routine losing all the entered information.

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10.1 INTRODUCTION

This program enables measurement results (RD files) or intermediate results (DI files, SM files and so on) to be drawn on a graphics terminal or a digital plotter for visual evaluation/interpretation. It is also possible with this program to compare data files with each other or with reference patterns. DI files and/or reference patterns can be added to or subtracted from each other.

When using this program, a graphics cursor can be used as an aid during evaluation, or to 'highlight' certain features and enter text on the plot.

Other Plot sub-programs are available in some of the other programs they are:

- SYSTEM PREPARATION, SYSTEMATIC ERROR CORRECTION program (refer to Chapter 7).
- SYSTEM PREPARATION, CALIBRATION program (refer to Chapter 7).
- DATA COLLECTION, during a scan (refer to Chapter 8).
- ANALYSIS, IDENTIFY (SANDMAN) program (refer to Chapter 11).
- ANALYSIS, LINE PROFILE program (refer to Chapter 11).
- ANALYSIS, QUANTIFY program (refer to Chapter 11).
- ANALYSIS, STRESS program (refer to Chapter 11).

10.2 PLOT

Up to four data files can be displayed graphically on a graphics terminal or on a plotter. The peaks (DI file) of one of the data files can be marked on the diagram.

On a graphics terminal with cursor, text and other information can be added to the display. The plot of a single data file can be used to edit the DI file of that data file.

First the name(s) of the data file(s) must be entered. The following file types can be plotted: RD, BK, PK, A2, SM, and 2D. You can choose another file type (same file name) by entering ".SM" or ".A2" and so on, for the file name. The default file RD or SM type can be chosen in Options/defaults.

If you choose the next default option: "PLOT", the system requests: "Starting angle" and "Final angle". If you work on a graphics terminal and have a plotter connected to the system then you can choose whether the plot is made on the terminal or on the plotter.
On a graphics terminal you return to the Plot menu (diagrams disappear from the screen) if you give RETURN (or "/" without RETURN).

10.2.1 THE GRAPHICS CURSOR

You can use a number of interactive features on the graphics terminal when the plot is finished. To operate these, first choose the cursor mode by typing "C". The graphics cursor can be moved over the screen by means of the arrow keys (for HP or VT240 terminals) or with the thumb wheels or the joy disc (Tektronix terminals). The following operations are now possible by typing the character (without RETURN):

I - Displays the intensity (in counts) at the position of the cursor with respect to the vertical or I-scale.

P - Displays the position of the cursor with respect to the horizontal or angle scale in degrees 2-theta. When a systematic error correction function was applied to the DI file, it is also applied on the cursor position.

T - Text mode. All characters typed after the "T" are displayed on a horizontal line at the cursor position. To choose another position for a following character, move the cursor. A RETURN terminates the text mode; the normal cursor mode is again active.

With the following cursor commands it is possible to edit a DI file. The files for the plot should all originate from one RD file, and a DI file must exist:

A - Adds the cursor position (angle and intensity) to the list of peaks in the DI file. If a systematic error correction function was applied to the DI file, it is also applied to the cursor position.

B - Overwrites the background value of the nearest peak in the DI file with the cursor position.

D - Deletes the peak nearest to the cursor position from the DI file.

E - (Not B!) Assigns the nearest peak to "Beta".

M - (Not A!) Assigns the nearest peak to "Amorphous".

O - Assigns the nearest peak of type "Other".

R - Replaces the peak nearest to the cursor position in the DI file with the cursor position. It combines the effects of D and A.

W - Overwrites the width of the peak nearest to the cursor position with a value equal to twice the distance between cursor and peak position.

1 - Assigns the nearest peak to "$Alpha_1$".

2 - Assigns the nearest peak to "$Alpha_2$".

3 - Assigns the nearest peak to "$Alpha_3$".

4 - Assigns the nearest peak to "$Alpha_4$".

* - Assigns the nearest peak to "$Alpha_*$". (Combined $alpha_1$ - $alpha_2$ peak.

? - Displays the peak type 0, 1, 2, 3, 4, *, A(morphous) or B(eta) at cursor position.

Peaks which have been added or modified by the commands A, B, E, M, O, R, W, 1, 2, 3, 4 or * are displayed in the DI file with U (User defined) instead of X in the line type columns.

After the command A or R the new peak has a width of 0.1 degree and a background value which has been interpolated between the values of the neighbour peaks.

For the commands B, D, E, M, O, R, W, 1, 2, 3, 4 and * the distance from the cursor to the nearest peak position must be equal to or smaller than the (old) tip width of the peak. The system warns you with a "BEEP" signal that the command is not executed when the distance is too large.

If a peak has to be added or replaced, you should use the following order of commands:

1. Add or replace the peak (A or R). $Alpha_1$ peak type is assigned by default!
2. Specify the line type if necessary (M, O, E, 1, 2, 3, 4 or *).
3. Specify the width of the peak if necessary (W). Default is 0.1 degrees.

The background (B) can be specified at any moment after A or R.

You return from the cursor mode to the PLOT menu if you give "/" (without RETURN). The diagram(s) disappear from the screen, or are scrolled off the screen, dependent on the terminal type you are using.

Text, intensity, angle position and peak type displayed on the screen are not stored in a memory. If you want to keep the results of your manipulations with the cursor, then make a hard copy before you return to the menu.

10.2.2 SECONDARY COMMANDS

DIAGRAMS, you can choose 1 or 2 diagrams (graphs) per plot or "automatic".

For two diagrams the angle range is divided into two parts. The second half of the graph is plotted under the first one on the screen or paper.

The default "auto" takes 1 diagram for less than a thousand data points per plot, 2 diagrams for thousand points or more. If the automatic choice is made the maximum angle width to be plotted in a single graph can be chosen.

I-SCALE, the default choice for the intensity full scale is "auto scale".

The scale is then determined from the highest data point of all the files to be plotted. The system chooses a value (of 1,2, or 5 x 10**n counts) just above the highest point.

You can choose any value in the range .01 - 50000(x1000) counts as full scale (this means: between 10 and 50 000 000 counts).

Then a choice must be made between "square root" and "linear" scale. The (default) square root scale has the property of displaying the background and small peaks in more detail than the linear scale with the same full scale value.

A multiplication factor for the counts of each file number can be selected for optimal surveyability.

GRAPH TYPE, for each file the line type of the graph can be chosen: Line, Dash, Segment, Point. The defaults for files number 1 up to 4 are in the same sequence. These four types of line are only available on a limited number of graphical terminal types (for example: 4014), if you have any other type of graphics terminal, only Line (this is also selected when you choose Dash or Segment) or Point are available.

The different line types are used to distinguish between the files. A graph of a raw data file can be more informative if you choose "Points".

On a multi-colour plotter the pen (colour) is chosen with the same number as the file. Lines are drawn faster than points or broken lines on a plotter, it is advisable to choose lines for all files to be plotted.

MARK PEAKS, peaks, as found by the peak search sub-program, can be marked on the graph for any one of the files.

Peaks can be marked by: Ticks, Lines, Angles.

Ticks are short lines near the zero (horizontal) axis, lines are written from zero to the top of the peak, angle values are printed together with lines.

If there are a lot of small peaks, then the angle values may obscure the small peaks and the other values.

Default is "Lines" which gives a very surveyable graph.

OPTIONS/ DEFAULTS With this command it is possible to permanently store selected settings for the above secondary commands. If you restart the Plot program, these defaults are read in and used.

Files : Define the default file name extension RD of SM. This extension will be proposed after starting the plot session, or taken if a filename without extension was typed in, while a filename had not yet been proposed.
Default = RD

Diagrams : 1, 2 or automatic
Default = automatic

I-scale : Automatic or manual choice of maximum intensity.
If you choose "manual" and there are more than one data files defined for plotting the system asks for a multiplication factor for each file.
Square root or linear scale.
Default = automatic choice for maximum intensity and square root scale.

Graph type : For any of four graphics, a type of line can be chosen from Line, Dash, Segment or Point.
Default = graph 1 : Line
graph 2 : Dash
graph 3 : Segment
graph 4 : Point

Mark peaks : Enter the file number for which peaks have to be marked (Default = 1).
If mark peaks is chosen, then specify how the peaks are to be marked, with ticks, lines or angles.

10.2.3 PLOT ON A PLOTTER

If you select the plotter to make diagrams on, the system asks the numbers of copies to be made when the plotter has been connected separately (via the queue manager), then the terminal returns to the menu dialogue when the plotter starts. A temporary plot file must first be prepared, this may take a minute.

On a terminal connected in parallel with the plotter, the dialogue resumes when the plotter has finished the plot(s).

Up to eight colours (pens) can be used, the pen number equals the file number. The actual number of pens to be used can be defined in System preparation, Assemble, System parameters, General. You should use "Lines" because it is faster than "Points" and improves the life of the pens.

If you have defined (for a Philips plotter) "No paper transport", then after each (copy of a) plot, the green light "DIGITIZE" is lit and the plotter waits. You may change paper sheets (Release/Hold), if you then press the button "SELECT" the plotter can commence with the next plot.

None of the cursor commands are available.

10.3 COMPARE

A program for visual comparison of data files with reference patterns.

Directly after entering the compare mode the menu is displayed with "FILE" as proposed choice because the data file name has to be entered first. Instead of a raw data (RD) file you may also enter a DI file, a smoothed data (SM) file, a background subtracted data (PK) file, or a file from which K-alpha$_2$ has been stripped (A2). The system expects either a RD file or a DI file as default, either of which can be chosen in Options/defaults. When a DI file is chosen the system can ask optionally if alpha$_2$ or amorphous peaks have to be plotted if available. These options can also be set in Options/defaults. If you should want another file type, but the same file name, you can choose that by entering ".SM" or ".A2" and so on (the file type extension), for the file name.

After entering the data file name the menu is displayed with "REF PATTERNS" as proposed choice.

Up to three reference patterns at a time can be plotted with the data file by entering their numbers. If you want to compare less than three reference patterns then give RETURN for the next number. If you want to compare more than three patterns you can do that in several turns. The system displays the reference patterns which you entered the last time as default the next time, you may delete a pattern number by entering zero.

After entering the data file name and a group of reference patterns the menu is displayed with "PLOT" as proposed choice.

The angle range of the file is displayed, then you can choose the starting and final angle of the graph. Default values are the angles of the file.

It is possible to change the Intensity scales of the data file and the reference patterns. Default values are: the normal scale value (1,2, or 5 times a power of 10) just above the highest point of the data file (always linear) and 100% for the reference patterns.

If you work on a graphics terminal and have a plotter connected to the system then you can choose whether the plot is made on the terminal or on the plotter.

On a graphics terminal, if the graph is finished you may enter "C" without RETURN to call the graphics cursor mode.

If you now type a character (without RETURN) it is written at the cursor position. The next character is written underneath the first unless you changed the cursor position. The system returns to the menu dialogue if you give RETURN or "/", the menu is displayed with "REF PATTERNS" as proposed choice. You can now enter the next group of reference patterns for comparison.

10.3.1 COMPARE ON A PLOTTER

If you select the plotter to make comparisons on, the system asks the number of copies to be made, when the plotter has been connected separately (via the queue manager), then the terminal returns to menu dialogue when the plotter starts. This may take a minute, a temporary plot file has to be prepared. None of the cursor commands are available for use.

For information about number of copies and number of pens refer to Section 10.2.3 "Plot".

10.4 ADD/SUBTRACT

DI files and/or a reference patterns can be added to or subtracted from each other. The initial pattern, the pattern to be added or subtracted, and the resulting pattern are plotted as stick graphs.

By repeating this action you can for example subtract step by step the reference patterns of the phases which have been identified with IDENTIFY (SANDMAN) or DI files of known substances.

First the initial DI file name must be entered. You have to define whether you want to add or subtract a DI file or a Reference pattern. The system then requests file name or reference pattern number.

You can choose whether you add or subtract the second pattern completely (100%) or a smaller percentage of it. You can choose a peak in the initial pattern to connect the percentage with. This is either the maximum peak of the second pattern or a peak at a specified angle or d value. An error window width (default = 0.1 degrees) can be defined. Peaks of the second pattern located within this 'window' distance from a peak of the initial pattern will be added to or subtracted from the initial pattern.

The system requests starting and final angle of the plot, default values are the starting and final angles of the initial file. The maximum value of the vertical scales of the patterns that can be chosen are: 1, 2, 5, 10, 20, 50 or 100%. The cursor mode can be used in the the same way as with COMPARE (refer to Chapter 10.3).

If you work on a graphics terminal and have a plotter connected to the system then you can choose whether the plot is made on the terminal or on the plotter (refer to Section 10.2.3). .

You can reduce the number of peaks in the initial file by deleting peaks smaller than a specified percentage, peaks outside a specified angle range, peaks with tip widths below a specified value or peaks with significances lower than a specified value.

The resulting pattern after addition or subtraction and/or reduction can be written to disc. Suggested file name is that of the initial file with the extension "Dn". Here "n" is a number from 1 to 9. The history (which patterns have been subtracted, what percentage, and so on) is not stored, so make a hard copies or send Add/subtract listings to the printer (or to an ASCII file).

Chapter 11. Analysis

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11.1 INTRODUCTION

Up to five optional programs can be used to analyse collected or pre-treated data. Those programs are:

- Phase identification (Search-match PW1861)
- Quantitative analysis (PW1863)
- Line profile analysis (PW1864)
- Crystallographic analysis (PW1865)
- Stress analysis (PW1868)

The results of one type of analysis may well be used as an aid (or condition) in another analysis program.

Analysis can be automatic (Identify and Quantify) or interactive.

11.2 IDENTIFY

11.2.1 INTRODUCTION

Together with the data collection, error correction, and peak search programs, the IDENTIFY program (SANDMAN) forms a powerful identification system. It is a computer search-match and identification program with a probability based scoring procedure.

The program originally ran on a Data General computer model NOVA, that is what gave it the name: Search AND MAtch on Nova. The program takes a DI file of an unknown substance and then searches the reference data base to see if a match occurs. The quality of the matches that are found is scored, and the match scores are listed in a match score table, this is more fully described in paragraph 11.2.7.2.

The DI file can have been generated as a result of the PEAK SEARCH command, or may have been manually entered (EDIT ALPHA1 PEAKS).

The reference data base to be used for the search-match procedure is displayed on the terminal, it can be any one of the following:

- The Powder Diffraction File data base (Inorganic), and
- The Powder Diffraction File data base (Organic), (together the PW1890)
- A User reference data base (assembled via the PW1862 program).

You choose the required data base by entering the device and UFD where the data base is stored (Options/defaults).

To get into the IDENTIFY mode, you must give "I" when you are in the ANALYSIS menu, this will then allow you access to the optional commands in the IDENTIFY mode.

11.2.1.1 References

1. W. Schreiner, C. Surdokowski, R. Jenkins. "A new minicomputer Search/Match /Identify program for qualitative phase analysis with the powder diffractometer." Journal of Applied Crystallography, Vol.15, 1982, p 513 - 523.

2. W. Schreiner, C. Surdokowski, R. Jenkins. "A probability based scoring technique for phase identification in x-ray analysis." Journal of Applied Crystallography, Vol.15, 1982, p 524 - 530.

3. W. Schreiner, C. Surdokowski, R. Jenkins. "Automatically correcting for specimen displacement error during XRD Search/match identification." Advances in X-ray Analysis. Vol.25, 1982, p 231 - 236.

4. H.P. Klug, L.E. Alexander; "X-ray diffraction procedures for poly crystalline and amorphous materials"; 2-nd edition; (1974); John Wiley & Sons, New York, etc.

11.2.2 OPTIONAL COMMANDS

The optional commands within the IDENTIFY (SANDMAN) program are as follows:

NEW DI FILE	(DI file name)
RESTRICTIONS	None Hard + dialogue Soft + dialogue
CHEMISTRY	Dialogue
KNOWNS	(ss-nnn) Reference pattern number(s)
SEARCH	Major phases Residue Isotypical Single Line
IDENTIFY	
MATCH	(ss-nnnn) Reference pattern number
LIST	Reference pattern (ss-nnn) Reference pattern number DI file (file name) Sub file (file name) Match score (file name) (minimum score) Line match (file name)
PLOT	(DI file name)
EDIT ALPHA1 PEAKS	+ Dialogue
OPTIONS/DEFAULTS	Representation Listings Data base Knowns

11.2.3 NEW DI FILE

This command specifies the name of a DI file which will be the input for following SEARCH, IDENTIFY, MATCH, or KNOWNS commands. The name remains in effect until a new file name is entered.

The DI file can be the output of the peak search sub-program, or can be entered manually by means of the EDIT ALPHA1 PEAKS command.

NOTE: If the file is the result of peak search (at a non-A2 file), then, after reading the file the system will remove the K-alpha$_2$ assigned peaks and recalculate each K-alpha (1 + 2) peak to its K-alpha$_1$ position and corresponding intensity. Refer also to Chapter 13.2.3.

Finally up to 127 K-alpha$_1$ lines are stored as the ´measured pattern´ for use in phase identification.

11.2.4 RESTRICTIONS

Normally the phases that are possibly present are more or less known, therefore the search can be performed on relevant reference patterns. The command RESTRICTIONS is used to set or clear search restrictions.

A restricted part of the data base can be specified as a subfile using the program SYSTEM PREPARATION, REFERENCE DATA BASE, or in this program using the subfile RESTRICT.SF.

Sub commands for RESTRICTIONS are:

None, Hard, Soft

11.2.4.1 None

With this sub command no search restrictions are in effect. The FEPS (Frequently Encountered Phases) file will be searched in the first pass and the rest of the data base in the second pass.

11.2.4.2 Hard

With Hard search restrictions in effect, only the subfile is searched. Paragraph 11.2.7.1 explains the search restrictions more fully.

11.2.4.3 Soft

With Soft search restrictions in effect, the patterns in the subfile are searched in the first pass and in the second pass the FEP file is searched to look for obvious matches. Patterns that are matched, but are not in the subfile, are marked with a X behind the Data mark in the match score table. Also, their match score is decreased, and therefore only good fits will appear in the table, they will not be identified in the IDENTIFY command.

11.2.4.4 Dialogue to Specify Search Restrictions

Restrictions are applied as a result of a dialogue as follows:

Restrictions subfile name: If you enter a subfile name, the search is restricted to the parts of the data base specified in the subfile. The contents of the subfile is displayed by the system.

If you enter "?" instead of a Restrictions subfile name, a directory of all subfiles in your UFD will be displayed.

If you entered "RESTRICT" for the subfile name the system will request: "Accept, Change, Delete." If you choose "Change" then the dialogue continues:

Minimum quality: Six quality (data) marks of reference patterns. The marks range from: Star, Calculated, Indexed, Blank data (no mark), Questionable data and "No restrictions" (all patterns included). If one of those marks is chosen, only reference patterns with data marks equal to or better than the chosen one are included in the search.

PDF subfiles: If the question is answered with No, the dialogue jumps to the next section, or, if Yes, you can select one or more of the PDF subfiles: Organics, Inorganics, Minerals, Non-minerals, Frequently Encountered Phases (FEPS), National Bureau of Standards (NBS) patterns, and Alloys.

The logical ´AND´ function is used when more than one subfile is selected. For instance, when FEPS and Minerals are selected, the search will be restricted to patterns that are minerals and are also present in the FEPS file (the minerals in the FEPS file).

Lattice types: The lattice type has to be given with the crystallographic symbol:

C primitive cubic	O primitive orthorhombic
F face-centered cubic	P body-centered orthorhombic
B body-centered cubic	Q base-centered orthorhombic
T primitive tetragonal	S face-centered orthorhombic
U centered tetragonal	M primitive monoclinic
R rhombohedral	N centered monoclinic
H hexagonal	Z triclinic (anorthic)

? displays this table

The logical ´OR´ function is used when more than one lattice type is selected.

Elements/groups absent: Input can be any of the following absent elements/groups. (upper and lower case letters are accepted):

A. Any element name from H (1) to Bk (97).

B. One of the following functional groups:
H2O, OH, NH2, NH3, NH4, CN, NO2, NO3, PO3, PO4, P2O7, CO3, SO4, IO3, BO3, SeO3, SeO4, AsO4, CrO4, MoO4, VO4, UO2, ClO4, WO4, BeF4, SiO4, ReO4.

C. LAN for all lanthanides: La (57) up to Lu (71).
ACT for all actinides: U (92) up to Bk (97).
- indicating a range of elements, where the range is indicated by a dash for example "H-Fe".

The logical 'AND' function is used when more than one element or group is selected. For instance, when Fe and Zn are selected to be absent, the search will be restricted to patterns that contain no Fe and no Zn.

NOTE 1: Elements present cannot be defined in "RESTRICT.SF". Use Chemistry, or assemble a subfile in REFERENCE DATA BASE (Chap. 7.4.2).

NOTE 2: The isotope D and the elements Cf and Es are not accepted as elements absent. They do however occur in some reference patterns. To exclude these elements, assemble a subfile of the type 'Ref patterns' refer to Chap. 7.4.2.

11.2

When two or more of the above four pattern characteristics are combined, the logical 'AND' function is used, for instance:

Minimum quality:	Calculated
PDF subfiles:	Minerals
Element/groups absent:	Cu

Patterns falling within these restrictions must have quality marks "Calculated" or better, and must be in the Minerals file, and may not contain Cu. In other words: the star quality and calculated mineral patterns, except for those containing Cu.

All the above specifications are assembled and saved in a file with the name RESTRICT.SF.

11.2.5 CHEMISTRY

Chemical information can be entered with this command. The program will ask:

Elements/groups present: The input can be names of chemical elements or functional groups (same as in command RESTRICTIONS). If you previously specified these elements, they will be displayed followed by: "Accept, Change, Delete all". All patterns that contain the specified elements are assembled in a file CHEMISTRY.SF. These patterns are searched in the first pass and will therefore get a higher probability to be selected than the others (refer to Chapter 11.2.7.1).

The file CHEMISTRY.SF should not be assembled/changed via the REFERENCE DATA BASE, ASSEMBLE SUBFILE, General command.

11.2.6 KNOWNS

Reference patterns of substances known to be present in the sample can be specified with this command. The reference pattern numbers are stored in the DI file. Maximum 5 patterns can be given. The patterns are marked with a "++" in the match score table. This is particularly useful when samples are measured with an internal standard. In the SEARCH program, known patterns are always scored first before other patterns are examined.

The knowns are used to calculate the specimen displacement error before the search begins.

When you choose KNOWNS, the system answers with a list of current knowns and asks the question:

"Accept, Change, Delete all = Change :="

If you choose change the system then asks:

"Propose: Current, Default knowns, Identified phases = Current :="

If any of the options are chosen the system proposes for the first known phase, the first one in the list of the chosen option.

The list of identified phases is the output of a previous IDENTIFY program.

The list of default knowns can be generated in OPTIONS/DEFAULTS.

If you do not want to delete all knowns, then choose "Change" and enter 0 (zero) for the pattern number that you want to delete.

NOTE: If you do not know any of the phases, but if you know that the displacement error has a certain value (for example: almost zero), then you can set this value using the Edit alpha1 peaks (Header) option. The value 0 (zero) means: EqDE is unknown (free), if you want to 'fix' the specimen height close to zero you have to define (+ or -) 15 micron.

11.2.7 SEARCH

The output of the search process is a Match score table on the listing device specified in Options/defaults. The results are also saved on disc in a MS file with the same name as the input DI file. This file can be used for later processing in IDENTIFY or can be shown on the terminal with LIST Match score.

The search sub-program can handle systematic shifts in the measured lines. The shift is treated as a free parameter and its magnitude is calculated in a least squares fit of the measured pattern to the reference pattern.

In a Major phase, Residue or Single line search, the line shift is assumed to be caused by a specimen displacement error (or errors that have the same effect on peak positions). It appears as an Equivalent Displacement Error (EqDE) in the output table.

In the Residue search, the lines of the patterns that are specified as ´knowns´, are subtracted from the user pattern before the Hanawalt-Fink search is executed. After the search, the original user pattern is used to match the found patterns.

In an Isotypical search, the line shift is assumed to be caused by a uniform change in D-value shown in the output table as delta-D over D (dD/D) in parts per thousand.

The Single Line option asks for the D-value or angle (specified in Options/ defaults) of the line to be searched and restricts the search to that line.

The search sub-program has two stages:

1. The actual search of the Hanawalt-Fink index file and
2. The ranking of the patterns found during the search stage by calculating their Match score.

11.2.7.1 Search Stage

All measured lines with 2 θ <85 degrees and intensities >10% of the strongest line are used in the first step of the search. If less than 15 lines meet these demands, lines with lower intensity are also used.

A Hanawalt-Fink index file is used for the search. It contains 7 lines for each pattern in the data base. The Hanawalt-Fink search method makes it unnecessary to inspect all the patterns in the data base. Each of the measured lines that are used in the first step of the search stage is compared with the strongest line of each reference pattern. If the measured and the reference line fit within a ´window´, that reference pattern is then selected for further inspection. The other six lines of the ´HF pattern´ are compared with all the lines of the ´measured pattern´. If sufficient lines (2 including the strongest line, 3 for Isotypical) fit, then for this pattern a preliminary score is calculated and patterns that fit (above search score cut-off) are saved in a table in the same sequence as their score. A maximum of 126 patterns can be saved.

A major phase search is executed in one, two or three passes, depending on the search restrictions, (refer to paragraph 11.2.4 "RESTRICTIONS"), and the chemistry indications (paragraph 11.2.5 "CHEMISTRY").

In the second and third pass through the data base during inspection the lines have to fit in a narrower ´window´ before they are selected for further inspection. The window width and the preliminary search score depend on the search restrictions and chemistry indications as indicated in table 11.1.

Table 11.1 Window Width and Search Score

Chemistry Y/N	Restrictions N/S/H	Search Pass	Through	Window width factor	Search score factor
No	None	1	FEPS	1	1
		2	rest of data base	0,5	0,6
	Soft	1	SUBFILE	1	1
		2	(rest of) FEPS	0,5	0,6 *
	Hard	1	SUBFILE	1	1
Yes	None	1	CHEMISTRY	1	1
		2	rest of data base	0,33	0,4
	Soft	1	CHEM ´AND´ SUBFILE	1	1
		2	rest of SUBFILE	0,33	0,4
		3	(rest of) FEPS	0,25	0,25 *
	Hard	1	CHEM ´AND´ SUBFILE	1	1
		2	rest of SUBFILE	0,33	0,4

* Additional FEPS patterns will become a Match score which is decreased by ´one third of the number of lines that hit´.

In an isotypical search, the chemical information is ignored. The search has always one pass. Without restrictions the whole data base is searched, and with restrictions only the selected subfile. It makes no difference if hard or soft restrictions are chosen.

The program displays the portion of the data base which is being searched. If you give "?" the system displays how many patterns and peaks have been processed at that time. A slash "/" can be given to terminate the search, the system will ask "Terminate? Yes, No" after having displayed how many patterns and peaks have been processed.

11.2.7.2 Match Stage

The start of the match stage is marked by the message "Matching ..patterns". The "?" and "/" commands can be used as described above. The reference patterns in the table are now scored with all their lines (the search uses only 7 lines). The result is given in a Match score table.

11.2.7.2.1 Match Score Table

Figure 11.1 shows an example of a match score table as can be displayed at the end of a search or with the "LIST" command. The information in that table depends on the choice that you make in OPTIONS/DEFAULTS: "Header listing: None, Short, Full". If you choose None, then only the data pertaining to the search-match-identification are listed. A short header also lists the data on the measurement. Full header means that all the data on the sample, the diffractometer, the measurement and the identification is listed.

This paragraph describes the data in the Full header:

* The first line tells you the type of table, the date and time.
* The second line displays the identification of the diffractometer system on which the measurement was done.
* The next four lines give the filename, the sample identification and the date and time of measurement.
* The next six lines display diffractometer number and specifics.
* The next line shows the analysis program, measurement range, and peak search parameters.
* The next twelve lines describe:
  - The type of search that has been performed
  - The date and time that the search began
  - The reference patterns defined as Knowns
  - The reference data base used to search/match
  - The number of K-alpha$_1$ peaks in the DI file, together with the number of peaks used in the search stage and the minimum value of I/I max. of these peaks
  - "Background Threshold". The background is calculated as BKG = CO + 2x square root (CO + BO), where CO is net counts and BO is background of weakest line in the DI file. BKG is normalized to the strongest line in the pattern

- The number of reference patterns in the data base, or in the part of the data base specified in the RESTRICTIONS subfile. Further the number of patterns "inspected" using the Hanawalt/Fink search method and the number of patterns that "scored" above the cutoff value with the search scoring algorithm are displayed
- If restrictions were imposed during the search, the name of the restrictions subfile and the level of restrictions (soft, hard) are displayed
- The number of phases identified is shown
- The last line of the header gives the number of patterns in the match score table.

* The next group of lines are the Match Score Table itself. The headings for the table are as follows:

No — Sequence number of the reference pattern in the Match Score table.

Match score — Maximum Likelihood Match Score, ranging from -25.5 to +25.5 (after Identify).

Add — Additive Match Score, refer to paragraph 11.2.7 "Identify".

Number of
- Ht — number of reference lines that are also in measured pattern (Hit).
- Ms — number of reference lines that are not in measured pattern (Miss).
- Bk — number of reference lines below background level of measured pattern (Background).
- Um — number of reference lines outside scan range of measured pattern (Unmeasured).

EqDE — Equivalent Displacement Error. In order to fit the reference pattern, all lines had to be shifted an amount that is equivalent to a specimen displacement of (EqDE) micrometer.

NOTE: In an isotypical search the EqDE column is replaced by dD/D (delta-D over D), in parts per thousand.

I% — The scale factor applied to fit the reference intensities to the measured intensities.

Id — Identified phases are marked with "+" (after Identify), knowns with "++".

Ref. pattern — The number of the reference pattern in the REFERENCE data base.

Qm — The data mark which shows the quality mark of the pattern: *, C(alculated), I(ndexed), blank, "(questionable), D(eleted).

Sf — The PDF subfile to which the pattern belongs: I(norganic), O(rganic), M(ineral), D(ual: Inorg.-Organic).

Phase formula/name — Depending on the default selected, this column can display chemical formulas, or mineral names and formulas.

11.2.7.2.2 Interpretation of the Match Score Table

After the Match phase the Match Score Table can be judged to be a reliable phase identification provided that phases are present that have:

1. A Match score > 1/3 of the Number of Hts.
2. The EqDE of the patterns should not differ more than 100 micrometers.
3. I% values that tend to approximate concentration values.

The reported patterns should be related to your application. If this is the case, an Identification stage can be run. The Additive match score column indicates positive scores for all phases that contribute significantly to the explanation of the DI file in conjunction to the higher scoring phase.

NOTE: A large % preferred orientation if not expected indicates poor matches. High scores combined with low I% and large % preferred orientation values are possible when many lines are considered under background rather than being missed.

A final conclusion about the qualitative composition of the sample can be drawn using the provided match score and line match tables and common sense. Phases having positive Additive Match scores but no "+" sign allocated by the Identify command can be considered as being present as well.

The "Major Phase" Search really only reports the major phases present, for a minor phase search the "Residue" command can be used.

11.2.8 IDENTIFY

Input for the IDENTIFY command is an MS file with the same name as the current DI file. If that file does not exist, a Major phase search will be made before the Identify stage starts.

In the identify stage, the program looks for a combination of patterns from the MS file that best fits the total measured pattern. At the end of the identify stage a match score table is displayed, this match score table differs from the table described in paragraph 11.2.7.2.1 in:

- There are two extra lines in the ´header´ telling you the average EqDE of the identified phases, and the score of the composite reference pattern built from the identified patterns.
- In the table itself there are three changes:

  Identified patterns are marked with a "+" before the reference pattern number.

  A pattern that lists the strongest remaining unmatched user line is marked with an apostrophe " ' " after the Additive score.

  The additive phase identification algorithm takes the following form:

  (a) Select (identify) the first phase.
  (b) Score it (them if more than one phase is identified).
  (c) Add the remaining candidate phases, one at a time, to the identified phase(s).
  (d) Score the composite and subtract the score obtained in step (b). (This becomes the Additive Match score).
  (e) Select the next best candidate based on the new scores and any other suitable criteria.
  (f) Go back to step (b) until all phases are identified.

  Once a pattern scores below zero, it is not considered further as a candidate for successive identification passes and is never rescored. Its score at the time of its demise, however, is preserved for reference. (The match cut-off).

MATCH SCORE TABLE 27-JAN-86 9:16

PW1700 Automated Powder Diffractometer System 1

Listed MS file name	:	MINMIX.MS
DI file date	:	24-JAN-86
Raw data file name	:	MINMIX.RD
Sample identification	:	MINMIX
Measurement date/time	:	30-DEC-83 10:53
Diffractometer system	:	1
Generator settings	:	40 kV, 37 mA
Cu alpha1,2 wavelengths	:	1.54056, 1.54435 Ang
Step size, sample time	:	0.020 deg, 1.00 s, 50.00 s/deg
Monochromator used	:	Yes
Diversence slit	:	Fixed (1 deg)
Analysis program number	:	99
Peak angle range	:	15.000 - 75.000 deg
Range in D spacing	:	1.26532 - 5.9014 Ang
Cryst peak width range	:	0.00 - 2.00 deg
Minim peak significance	:	0.75
Type of search	:	Major phases
Search date/time	:	24-JAN-86 17:07
Reference data base	:	1985 PDF DL1:[300,57]
Number of Alpha1 peaks	:	62, 15 searched with I/Imax down to 8.9%
Background threshold	:	0.4%
Number of ref patterns	:	35204, 8977 inspected, 2793 scored
Nr of patterns matched	:	126 out of 292 above search score cutoff
Nr of phases identified	:	5
Average equiv displ err	:	33 micrometer
Total additive score	:	28.8

No	Match score	Add score	Number of Ht	Ms	Bk	Um	Eq.D.E (micron)	I%	Id	Ref pattern	Q	M	S F	Phase formula/name
1	9.0	7.5	21	0	2	16	45	27	+	5- 586	*	M		CALCITE, SYN
2	7.1	7.1	15	0	3	21	45	25	+	5- 490	D	M		QUARTZ, LOW
3	6.6	6.5	12	0	3	28	15	28	+	33- 664	*	M		HEMATITE, SYN
4	6.3	5.0	13	0	2	24	45	11	+	10- 173	I	M		CORUNDUM, SYN
5	5.2	-2.9	16	0	1	5	-30	23		24- 27	C	M		CALCITE
6	5.2	-4.6	16	1	1	20	15	56		33-1161	*	M		QUARTZ, LOW
8	4.4	-3.4	13	1	8	18	45	26		33- 960	*	I		NiTiO3
9	3.5	-0.4	12	0	3	4	-15	9		29- 354	*	I		CaNd2S4
10	3.1	-1.0	12	1	0	15	-15	8		26-1450	I	I		Nd2S3
11	2.6	-1.9	4	0	0	8	-15	22		4- 864	D	M		FLUORITE, SYN
13	2.4	-4.8	12	2	2	23	105	19		17- 617	D	I		NiTiO3
14	2.2	-1.1	5	0	3	12	-135	7		20- 314	I	I		Cr3Rh
15	2.0	-0.8	13	2	6	9	0	41		18- 89	*	I		NH4CoCl3
16	2.0	-1.4	9	0	1	14	75	9		34- 367	*	I		BaB6
17	2.0	-1.7	7	0	1	13	120	10		8- 411		I		KBiS2
18	2.0	2.6	4	0	2	10	15	25	+	35- 816	*	M		FLUORITE, SYN
19	1.9	-1.2	11	1	2	24	-15	12		32- 382	C	I		Eu3S4
20	1.8	-1.3	5	0	0	9	-120	11		19- 374		I		Co3V
21	1.7	-0.7	12	0	2	20	-105	4		32- 898	C	I		Rh3.92Se8
22	1.5	-0.1	5	0	2	14	-15	11		17- 23		I		Pd3Ce

Figure 11.1A Example of a Match Score Table

LINE MATCH TABLE 27-JAN-86 9:17

Listed MS file name : MINMIX.MS

Number of Alpha1 peaks : 62, 15 searched with I/Imax down to 8.9 %
Background threshold : 0.4%
Number of ref patterns : 35204, 47 above match cutoff, 5 identified
Average equiv displ err : 33 micrometer

Reference pattern :	5- 586	5- 490	33- 664	10- 173	35- 816
Source :	Identif	Identif	Identif	Identif	Identif
Match score :	9.0	7.1	6.6	6.3	3.6
Nr of Ht, Ms, Bk :	21, 0, 2	15, 0, 3	12, 0, 3	13, 0, 2	4, 0, 2
New nr of Ht, Ms :	22, 0	13, 0	9, 0	7, 0	3, 0
Equiv displ error :	45	45	15	45	15
I% (scale factor) :	27	25	28	11	29
Mat'l balance (%) :	23	22	24	9	22
Pref orientat (%) :	52	35	15	50	32
Minimum D spacing :	0.965	0.928	0.801	0.888	0.814

Dcorr (Ang)	I/Imax (%)	Used (%)	5- 586 dD/D *1000	5- 586 I (%)	5- 490 dD/D *1000	5- 490 I (%)	33- 664 dD/D *1000	33- 664 I (%)	10- 173 dD/D *1000	10- 173 I (%)	35- 816 dD/D *1000	35- 816 I (%)
4.247	7.6	110			-3	8.3						
3.855	1.5	219	-2	3.2								
3.681	7.1	117					-1	8.3				
3.478	5.6	148							0	8.3		
	1.3	48			-1	24.5						
3.10											0	22.4
3.033	10			26.9								
2.845	1.1											
2.732	-										Bk	0.2
2.700	33.9	81					0	27.5				
1.297	0.9	59	0	0.5								
1.288	0.9	111	4	0.3*	0	0.7*						
1.277	0.3	174							1	0.4		
1.260	-						Um	2.2				
1.256	-				Um	1.0						
1.253	-										Um	2.2
1.247	-		Bk	0.3								
1.239	-								Um	1.8		

Number of matched reference lines : 54 in common D range
Number of missed reference lines : 0
Number of unmatched peaks remaining : 8 with I/Imax up to 11%
Total I/Imax in user pattern (%) : 466
Total I/Imax used, remaining (%) : 308 (66%), 158 (34%)

Figure 11.1B Example of a Line Match Table

The identification algorithm employs several criteria in selecting phases, other than merely the Additive match scores. These include an acceptable range of the displacement error values, the number of new user lines hit by the candidate, the number of unhit lines remaining in the unknown, and so on. After a candidate is selected as an identified phase, it is rescored with less stringent hit requirements (for example: 25% instead of 40% hit probability). This is what a human analyst would do, once he became convinced a certain phase was present, because line interference effects may be obscuring an otherwise good match.

The first item that you will notice in the LINE MATCH TABLE is the header. Essentially, it breaks down the search parameters, such as how many lines ($Alpha_1$ peaks) were available, the background threshold, how many initial patterns were in the data base, and the number of patterns above match cut-off and identified. The last line of the header shows the average equivalent displacement error.

11.2

If Full listings were defined in Options/Defaults, then the line match table contains all lines of the measured pattern together with the corresponding lines of the identified patterns.

Below this are columns where each reference pattern match is explored in detail; such as the match score of this reference pattern, the number of hit, missed and background lines, the number of new hit and missed lines, the Eq.D.E., and the scale factor (I%). Two new items, the PREFERRED ORIENTATION, and the minimum referenced d-spacing available on the reference pattern are displayed.

The PREFERRED ORIENTATION score indicates how well the reference pattern accounted for the intensities of the lines it matched. For randomly oriented phases, this score can be between 10% and 30%. In cases where the percentage PREFERRED ORIENTATION is higher than 30%, it indicates that the phase is preferredly oriented.

When the value of the minimum referenced d-spacing is greater than the smallest d-spacing on the pattern, the reference pattern does not have as many lines as the measured pattern could provide. This will not hinder the search in any way, only lower the possible Match score that the phase could attain.

Below this sub-header the user pattern is broken down by lines (if Full data listing was defined in Options/defaults. The lines of each reference pattern that matches are indicated. The first three columns represent the lines from the user pattern. The d-spacing corrected for displacement error (average), normalized intensity, and the percentage used (used I%) by the reference pattern are displayed. Under the reference pattern number you will find two quantities for each matching line; the dD/D (delta d/d in parts per thousand) and the scaled intensity. The dD/D represents the error of the line. Normally this error would be within $\pm$ 3 parts per thousand for a line, but higher values do not necessarily indicate bad matches. The scaled intensity is simply the intensity from the card (reference pattern), multiplied by the scaling factor (I%).

If an overlap of two or more cards or lines from the same card occur, the intensities are labelled with a "*" for each line. Misses -lines present in the reference pattern but not in the user pattern- and background -lines present in the reference pattern but not in the user pattern because of their low intensity- are labelled as separate lines in the user pattern where they would have been observed. Unmeasured -lines of the reference pattern outside measured range- are also displayed in this way.

If the user pattern has lines outside the limits for the reference patterns, the table will indicate this by displaying a broken line across the first column to show the end of the common d range. Thereafter, all lines for this reference pattern are unknown, and the table labels them with an "-" in both columns. This will continue for the rest of the user pattern.

At the end of the table a summary appears. This summary reports the number of lines actually matched out of the number of possible matches, how many reference lines were missed, how many lines remain unmatched, and the maximum I/I max. of these lines. The amount of total intensity matched, and unmatched, is displayed as a percentage. The next logical step would be to evaluate the match to see if there are any knowns that you can pick out that the program cannot. If there are, enter them as KNOWNS, and re-run the search. If not, the only conclusion that can be made is that the phases not yet found are not part of the data base.

11.2.9 MATCH

This command can be used to see how well (a) specific reference pattern(s) fit(s) a measured pattern (a maximum of 10 reference patterns can be matched in one turn). A MS file of the given name must be present. Output is a match score table and a line match table on the terminal. The pattern which has been matched is marked with ++ in the match score table.

11.2.10 PLOT

In this routine you can plot the DI file data, up to five different reference patterns and a composite pattern of these reference patterns.

The phases identified by a "+" or "++" in the identification routine are plotted by default. The plot percentage value used is the same as the normalized intensity of the strongest line of the reference pattern in the user pattern. It is possible for you to change the plot percentage.

11.2.11 LIST

Command to show on the terminal: a Reference pattern, a DI file, a Sub file (refer to Chapter 7.4.7), a Match score table or a Line match table.

For the Match score table an additional parameter is the minimum Match score value to be displayed. Range from -25.5 to +25.5, default is 0.

11.2.12 EDIT ALPHA1 PEAKS

By means of this command an existing DI file can be modified or a new DI file can be entered manually via the keyboard. The representation of peak position and intensity is defined in OPTIONS/DEFAULTS. For more details about this command refer to Chapter 9.3 "EDIT ALPHA1 PEAKS" (PATTERN TREATMENT).

11.2.13 OPTIONS/DEFAULTS

You can define the defaults for four groups of parameters or options.

11.2.13.1 Representation

Peaks can be shown or entered (represented) as d-spacings or 2 theta Angles. Refers to the commands LIST DI file, LIST Reference pattern, and EDIT ALPHA1 PEAKS.

Intensities can be shown or entered (represented) as Counts or Normalized. Refers to the commands LIST DI file and EDIT ALPHA1 PEAKS.

Names of patterns can be printed as chemical Formula or as Mineral names. Refers to Match score table and LIST Reference pattern command.

11.2.13.2 Listings

Listings can be Full, Short or Optional, this is true for the Header as well as the data. Refers to Match score table and Line match table:

A short Header skips the information on diffractometer and generator.

A Short Match score table skips patterns outside the restrictions subfile and patterns that have large EqDE values.

A Short Line match table skips the whole user pattern and shows only the header and trailer lines (the summary).

Output can be sent to the Terminal, to the Printer or it can be written on file. Refers to the Match score and Line match tables.

NOTE: The parameters (peaks, intensities, listings, output, names) are saved on disc (in your UFD). The last given value is effective, even after restarting the program.

11.2.13.3 Data Base

You can choose another reference data base (Device and UFD) for phase identification. This data base remains in use until you change it using Options/defaults again, in Analysis, Identify or in System preparation, Reference data base.

11.2.13.4 Knowns

You can generate your list of default knowns in the same way that you generate your list of current knowns (refer to Section 11.2.6). This list is also used during the automatic identification procedure (refer to Chapter 7.2.3.4).

11.3 QUANTITATIVE ANALYSIS

11.3.1 INTRODUCTION

For routine operation, use is made of an Automatic Analysis Procedure. After data collection, the calculations and output are performed automatically.

The analysis programs contain the measurement parameters for the phases together with background and line overlap corrections, and the calculation model with calibration constants.

Alternatively, already collected data (QI files) can be analysed using the Addition type of analysis program, without the need of calibration.

A complete quantitative analysis procedure consists of two main parts:

* System preparation - ASSEMBLE GONIO SCANS, PHASES and ANALYSIS PROGRAMS
  - CALIBRATE
* Data collection and analysis - DATA COLLECTION combined with analysis and output in the Automatic Analysis Procedure

NOTE: Calculations using QI files of original and enriched samples with the Addition method can only be done interactively (refer to Section 11.3.9).

The following text describes these main parts:

SYSTEM PREPARATION

- ASSEMBLE a GONIO SCAN (refer to Chapter 7.2.4) for the angular range 10 - 60° degrees 2θ, and an ANALYSIS PROGRAM, Scans only.
- DATA COLLECTION according to these scans on 1 - 4 standard samples.
- Use the PLOT and COMPARE facilities to determine the appropriate PEAKS and/or AREAS to be assembled in PHASES.
- In PLOT mode the cursor can be used:
  a. by using the key "P" to find the exact position of peaks, background and starting and final angles to enter in phase assembly
  b. to determine the overlapping phases, the overlap factor and constant background values (key "I")
- ASSEMBLE the PHASES and the ANALYSIS PROGRAM, Quantitative (refer to Chapters 7.2.3 and 7.2.5) using information determined above.
- DATA COLLECTION on standard samples according to the quantitative ANALYSIS PROGRAM
- CALIBRATE (refer to Chapter 7.5) by:
  a. ASSEMBLE CALIBRATION SET (input of concentrations)
  b. INPUT QI FILES previously produced
  c. CALIBRATE to calculate the calibration constants
  d. PLOT the calibration lines of the analytical phases to see the results

DATA COLLECTION AND ANALYSIS

- DATA COLLECTION of QI files using the ANALYSIS PROGRAM assembled above, and the quantitative results calculated will be sent to the printer.

CALCULATE

- CALCULATE and output the concentration of the analytical phase from the QI files using the Addition type of ANALYSIS PROGRAM.

- CALCULATE anew the quantitative composition using an existing QI file and another ANALYSIS PROGRAM if you think that is more appropriate.

Section 11.3.12 describes the procedure in more detail (step-by-step).

A complete sequence of quantitative analysis is given as a 'worked example' in Appendix D.

11.3.2 PRINCIPLES OF QUANTITATIVE ANALYSIS

The intensity of a diffraction peak of a chemical compound is dependent on the structure and elements of the compound, the diffractometer characteristics, the weight fraction of the compound in the total sample, and the absorption coefficient of the sample. If the sample is not infinitely thick, then the thickness and density of the sample layer (its mass) may also influence the intensity. This means that we can establish the weight fraction or concentration by measuring the intensity of at least one peak of the compound, by multiplying this intensity with a proportionality factor or calibration constant for this compound in this diffractometer, taking into account the mass absorption coefficient (or mass attenuation coefficient) of the sample. In thin samples the transmission of the layer must be accounted for, then the mass or the concentration can be determined.

This can be expressed in the following formulas:

Concentration:

$$C_i = B_i \times I_i \times MAC$$

This is the formula used in the 'General calculation' model. In this formula:

C_i is the concentration or weight fraction of compound i
B_i is the calibration constant of compound i in the relevant diffractometer
I_i is the net intensity of (a) peak(s) of compound i
MAC is the mass absorption coefficient of the sample (mixture of compounds)

Mass

$$M_i = B_i m \times I_i \times \ln\left(\frac{1}{T}\right)$$

This is the formula used in the 'General calculation' model. In this formula:

M_i is the mass of compound i in the thin sample
$B_i m$ is the calibration constant for mass of compound i
I_i is the intensity measured on a thin sample, then converted to 'thick' sample value
T is the transmission factor of the thin sample layer

Each of these factors will be discussed in the following chapters.

11.3.3 INTENSITY MEASUREMENTS, PHASES

In APD1700 the measurement parameters of a diffraction peak for quantitative analysis are defined in a Phase (refer to Chapter 7.2.5 Assemble Phases). We distinguish two types of phases (two different ways to establish the intensity of a peak) these two types are: peak phases and area phases.

P = peak angle
S = starting angle
F = final angle
delta(2θ) = angle difference = (F-S)

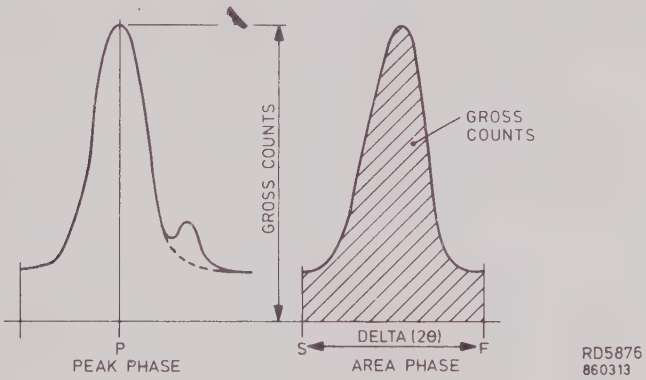


Figure 11.2 Peak and Area Phases

With a Peak phase, the gross phase counts are measured for a specified time at the angle of the peak's maximum. This angle can be an absolute input angle, or the actual maximum as found after a search. The gross intensity is the gross counts divided by the measuring time.

The gross intensity measured with an Area phase is the gross phase counts integrated during a scan from a starting angle to a final angle at a specified speed, divided by the measuring time and multiplied by the angle difference delta(2θ).

$$I_{gross} = \frac{\text{phase counts}}{\text{meas. time}} \times \text{delta}(2\theta)$$

By using the intensities as described above, the measurement (for example, the counting statistical precision) can be improved by changing measuring times or speed (or even delta(2θ) if required), while the calibration constants remain the same.

11.3.3.1 Background Correction

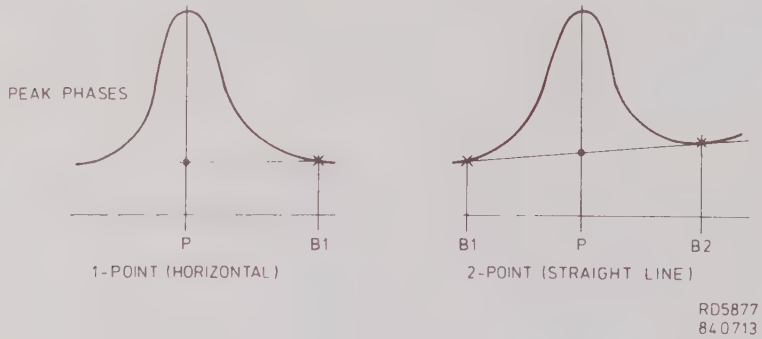
For both types of phase the gross intensity can be corrected for background by measuring for a specified time at one or two angle positions.

For each background measuring point, the background intensity is calculated first:

$$I_b = \frac{\text{background counts}}{\text{background time}}$$

Then the background correction is calculated (refer to figure 11.3). For peak phases the background at the peak position (P) is interpolated from the background points:

$$\text{Bkg. corr} = I_{b1} + (I_{b2} - I_{b1}) \frac{P - B1}{B2 - B1}$$



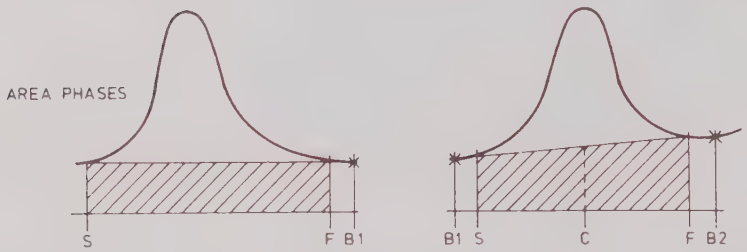


Figure 11.3 Background Interpolation RD5878 840713

For area phases the background at the centre of the area:

$$C = S + \frac{\text{delta}(2\theta)}{2}$$

is interpolated from the background points and multiplied by the angle difference:

$$\text{Bkg. corr} = \{I_{b1} + (I_{b2} - I_{b1}) \frac{C - B1}{B2 - B1}\} \times \text{delta}(2\theta)$$

The background corrected intensity is:

Icorr = Igross - Bkg.corr

NOTE 1: The positions of peak and background measuring angles, and of starting and final angles can be found easily with the aid of the Graphics, Plot program, using the cursor and the P (position) command on (a) raw data file(s) of (a) representative sample(s), refer to Chapter 10.2.

NOTE 2: Another type of background correction can be used if the background is a constant or if it has a constant curvature, refer to Chapter 11.3.3.7

11.3.3.2 Search for Maximum

You may require the instrument to make a search for the maximum of the peak before the actual measurement of the phase starts. Then the goniometer will make a specified number of steps below and above the peak angle, or around the centre of the area, making a measurement for a preset time after each step. The centre of the area is found by the formula:

$$S + \frac{\text{delta}(2\theta)}{2}$$

After this small step scan the difference between the real and the specified angles is calculated. All further measurement angles for the same phase (peak, background, starting and final angles) are shifted over the calculated difference.

For Peak phases it is advisable to <u>always</u> use the maximum search. For Area phases it is not necessary and in fact has the disadvantage that you must specify a ´symmetric´ area scan, because the maximum is searched around the ´centre of the area´.

11.3.3.3 Thin Sample Conversion

Quantitative analysis of a thin sample is somewhat more complicated than quantitative analysis of an ´infinitely´ thick sample. In the latter case the weight fractions of the phases in the mixture are unknown, together with the mass absorption coefficient of the sample. For thin samples the thickness and the density of the powder layer are further unknowns.

Thin samples can be mounted on polycrystalline plates (for example: Ag membrane filters) or on mounting plates which will not themselves produce peaks (for example: glass plates, polymer membrane filters, obliquely cut single crystals). The intensity of a diffraction line of a thin sample is:

$$I_{it} = I_i \left(1 - e^{-\frac{2\mu\rho t}{\sin\theta_i}} \right)$$

In this formula :

I_i	=	intensity of the same line in an "infinitely" thick sample
μ	=	mass absorption coefficient
ρ	=	density of the sample
t	=	thickness of the sample layer
θ_i	=	diffraction angle of the line "i".

Before mass or concentration can be calculated the intensity measured at the thin sample is converted into an intensity as if measured on a thick sample. This intensity conversion is done after background subtraction and before overlap correction. The converted intensity is:

$$I_i\text{conv} = \frac{I_i\text{corr}}{1 - T^{S_i}} \quad \text{in which} \quad \frac{1}{1 - T^{S_i}} = \text{´conversion factor´}$$

Here is $T = e^{-2\mu\rho t}$ = "transmission factor" of the sample layer

$S_i = \frac{1}{\sin\theta_i}$

The transmission factor T can be determined in two ways. For a polycrystalline plate we measure the intensity of a line of the 'clean' plate (I_p0) at angle θ_p. Then the same line of the dust-covered plate (I_p) is measured. This peak should be free from line overlap from any of the sample peaks. From figure 11.4a it can be seen that the plate intensity ratio:

$$\frac{I_p}{I_p0} = e^{-\frac{2\mu\rho t}{\sin\theta_p}}$$

Therefore the transmission factor will be:

$$T = \left(\frac{I_p}{I_p0}\right)^{\sin\theta_p}$$

If you measure the clean plate with an analysis program of the type "Thin sample, Plate measurement only" the net intensity will be stored in a special file type with the extension QP. For the analysis of the sample layer deposited on this plate, the analysis program should contain the same plate reference phase.

The system recognizes two ways of using a polycrystalline sample plate: Individual or Universal.

The "Individual plate" option is used if each sample is mounted (collected) on its own (filter) plate which was previously measured and labeled as clean plate. In this case the QP file with the same name as the QI file of the sample is chosen by default in automatic analysis procedures. In interactive calculations, the QP file name suggested is the same as the QI file of the sample.

The "Universal plate" option is used if you have only one plate which is used as a 'support' for (for example) polymer membrane filters. In this case automatic analysis procedures use the QP file name as stored in DEFAULTS.APD. In interactive calculations, the same name is suggested. If you change the name of the universal plate file in the dialogue following the CALCULATE command (in ANALYSIS, QUANTIFY), the new name will be stored in your defaults file. When you start using the universal plate thin sample analysis method for the first time the system will give this file the name "UNIVERSAL.QP". You may give the clean plate this filename during its measurement, or you have to change the name while doing an interactive calculation of the thin sample.

If considerable time elapses between measurement of clean plate and mounted sample, then you should use the monitor ratio to compensate for intensity changes between measurements (refer to Section 11.3.8). If you measure the sample shortly after the clean plate, it is not then necessary to do monitor measurements if you are using the relative type of concentration calculation.

For amorphous or single cystal plates the previous method cannot be applied. It also cannot be used if the sample does not completely cover the irradiated area. In these cases we propose the following solution: Choose one of the components of the sample as the "Reference compound". The reference compound should be contained in all the samples in reasonable concentration (it can of course be the compound to be analysed). Measure the intensity ratio of two lines of the reference compound (I_{1t} and I_{2t}) in the thin sample see figure 11.4b. Peaks 1 and 2 should be free of line overlap.

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$$\text{intensity ratio factor} = \frac{I_{1t}}{I_{2t}} \times \left(\frac{I_2}{I_1}\right) = \frac{1-T^{S1}}{1-T^{S2}}$$

Here: $\frac{I_2}{I_1}$ is the intensity ratio of the two reference lines measured on "infinitely" thick sample(s) for calibration.

And so: T can be determined (by iteration) using the θ-dependence of the transmission.

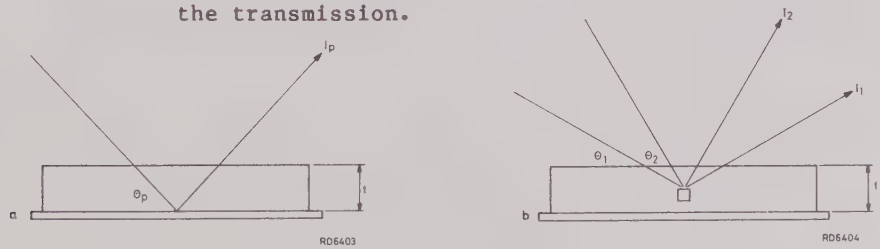

Figure 11.4 Thin Sample on Mounting Plate

If you use an analysis program with a relative type of concentration calculation, it is not necessary to do monitor measurements.

Before intensity conversion and further calculations are performed, the significance of the intensity ratios used to determine the transmission factor are checked.

If the plate intensity ratio is not significantly smaller than 1, the system will display: "This might be a clean plate" and "Concentration/mass calculation cannot be performed.

If the plate intensity ratio is not significantly larger than 0 (zero), or if the intensity ratio factor for the two reference lines is not significantly larger than 1, then the system will display the message: "This might not be a thin sample".

For an analysis program for mass calculation the system will display: "Mass calculation cannot be performed".

For analysis programs for concentration calculation the message will be: "Thin sample conversion will not be performed". The system will do subsequent calculations as if this were a thick sample.

In all other cases the converted intensity will be corrected for line overlap if necessary. Subsequently mass calculation can be done, or concentration calculation as with 'thick' sample intensities.

11.3.3.4 Overlap Correction

The line overlap correction feature in the Analysis program can be used in the same way in two different situations, refer to Figure 11.5 a and b.

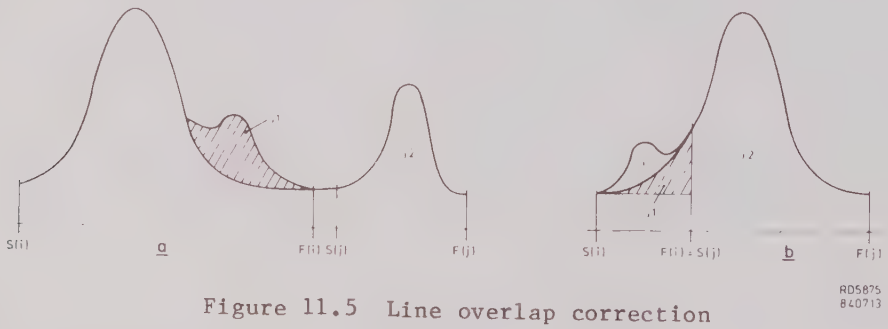

Figure 11.5 Line overlap correction

In situation a the compound to be analysed (peak i) is overlapped by a peak of compound j (peak j1). For the correction method to be applicable we expect that the intensity ratio I_{j1}/I_{j2} is a constant. This means: we assume that there is no preferred orientation problem for compound j. Also j1 and j2 can be two different orders of reflection for the same set of lattice planes (for example the (110) and (220) lines will be equally influenced by preferred orientation).

You can establish the ratio I_{j1}/I_{j2} by measuring a sample of pure j (or a sample where no overlap for peaks j1 and j2 occurs). The net intensity for peak i is then:

$$I_i = I_i corr + F1 \times I_{j2} corr, \text{ in which } F1 = \frac{I_{j1} corr}{I_{j2} corr}$$

For a thin sample the intensity converted to a value as if measured on a thick sample ($I_i conv$) is used instead of the background corrected intensity ($I_i corr$).

It is possible to do line overlap correction in this way for up to 4 overlapping phases (using F1 to F4).

It is not allowable to correct phase i for phase j and at the same time correct phase j for phase i. In that case the system - during Assemble, Analysis program - will display a message:

"Overlap correction of phase j and i to each other"
"New analysis program will not be stored"

You must choose either another overlapping phase, or another analytical phase (another peak of the same compound).

In situation b (figure 11.5 b) we want to establish the net intensity of phase i which is strongly overlapped by a large peak j2. If peak j2 is (practically) constant in all samples, then you may use the constant background correction method described in chapter 11.3.3.7. If I_{j2} is not constant, then you can use the method as described for situation a. For Area phases F(i), the final angle of phase i (+j1) will in general be equal to the starting angle of phase j2, or S(j).

An overlapping phase can be deleted by entering "0" (zero) for the "Overlapping Phase Number". The method described above can be used for overlap correction of Area phases as well as Peak phases. It will work equally well for a combination of Area and Peak phases.

11.3.3.5 Non-random Orientation

The overlap correction method can sometimes be used for intensity correction in the case of non-randomly oriented compounds.

Use an (almost) random sample to establish the intensity ratios between up to a maximum of five peaks of the same compound i. The factors F1 to F4 (intensity ratios I_{i1}/I_{i2} up to I_{i1}/I_{i5} respectively) will be positive so that the corrected intensity equals the weighted sum of (up to) five peaks:

$$I_i = I_{i1}corr + F1 \times I_{i2}corr + F2 \times I_{i3}corr + ...$$

NOTE: For this method you must choose peaks representing different sets of lattice planes (not different orders of the same plane).

11.3.3.6 One Background for Several Phases

If you want to use only one background measurement for several phases (in order either to save time, or because this is the only real background point in the region) then you can use the line overlap correction procedure for this purpose. Assemble a special ´phase´ for the background measurement. Choose: Peak phase, no background, no overlap.

For the analytical phases, assemble Area or Peak phase, no background. Enter the special background phase as overlapping phase. The overlap factor F1 must be:

- for Peak phases : 1
- for Area phases : delta(2θ), the difference between starting and final angle (degrees).

11.3.3.7 Constant Background Correction

In the Analysis program you can enter a constant background correction (b) for each phase. It can be used not only for correcting a constant background, but also for a constant line overlap or a (constantly) curved background.

The correction constant for phase i can be established by means of the Plot facility in Calibration (refer to System preparation, Chapter 7.5) or by measuring a sample which does not contain phase i (refer to Figure 11.6).

For a constant background, the phase can be assembled without background measuring points (zero points). If you have to correct for a constantly curved background (or overlap), then use of two background points is the most logical choice.

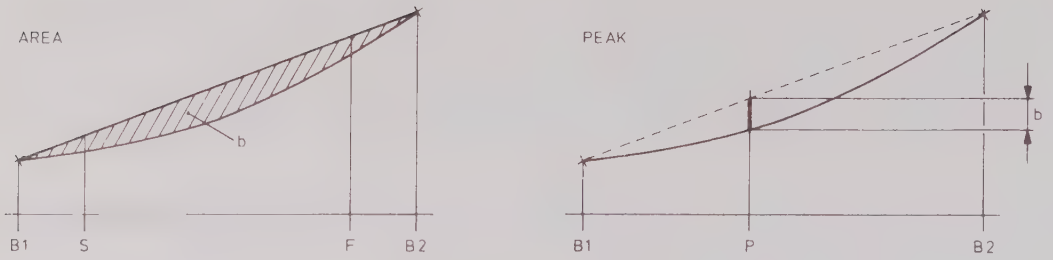

Figure 11.6 Constant background correction

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For a concave background as in figure 11.6 the background correction b will be positive, for a convex background b will be negative.

The complete formula for the net intensity (for phase i) is:

$$I_i = I_i corr + b + F1 \times I_j corr + F2 \times I_k corr + F3 \times I_l corr + F4 \times I_m corr$$

11.3.4 CALIBRATION CONSTANTS

Calibration constant is the name for the proportionality constant used for converting net intensity into weight fraction or concentration, or mass of a thin sample layer. It is built up from the following factors:

- Constants of the chemical compound such as:
  structure factors, absorption coefficient, diffraction angle.
- Geometrical constants: Lorentz-polarization factor, which is a constant for the specified diffraction angle.
- Instrument constants such as slit dimensions, irradiated area of the sample, "sensitivity" of the detector.

NOTE: The tube intensity is not constant, this will normally be compensated for by using the intensity ratio to either an external monitor sample or an internal standard or reference material.

Calibration constants are established by measuring standard samples with known concentrations or masses (refer to Chapter 11.3.4.1). The Calibration program (System preparation, described in Chapter 7.5) requests an Analysis program number for the calculations. In the Analysis program is defined which are the analytical and overlapping phases, and which calculation model is to be used (refer to Chapter 7.2.3, Assemble, Analysis program).

Which model is to be used depends mainly on the way you want to deal with the mass absorption coefficient of the sample (refer to Chapter 11.3.5, MAC). We can distinguish three types of calibration constant for concentration calculation:

- absolute: $B_i = \frac{C_i}{I_i \times MAC} = \frac{1}{I_i 0 \times MAC_i}$, used for the General model.
  $I_i 0 = I_i$ at pure phase i.
  MAC_i = MAC of phase i

- straight line: $B_i = \frac{C_i}{I_i} = \frac{1}{I_i 0}$, used for the Straight line model.

- relative : $B_i = \frac{C_i}{C_s} \times \frac{I_s}{I_i} \times B_s$,for the Internal standard model.

C_s = concentration of internal standard phase
B_s = calibration constant of internal standard = 1.0

$$B_i = \frac{C_i}{C_r} \times \frac{I_r}{I_i} \times B_r$$, for the Matrix flushing and Binary models.

C_r = concentration of reference phase
B_r = calibration constant of reference phase = 1.0.

The calibration constant for mass calculation is:

$$B_im = \frac{M_i}{I_i \times \ln(\frac{1}{T})} = \frac{M_i}{I_im}$$

in which: I_im = "mass related intensity"

11.3.4.1 Calibration standard samples

You may use one or more (maximum 25) calibration standard samples for the calibration of the system for a number of phases. If you use more than one standard samples, then linear regression analysis will be applied by the system to establish the calibration constants.

11.3

NOTE: The system uses net intensities for the calculation of the calibration constants. If applicable you must therefore first determine (off-line) the line overlap factors (F) and/or the constant background corrections (b) before you can start the calibration.

If more than one standard sample is used, then each sample does not necessarily have to contain all the analytical phases. For absolute and straight line calibration constants, the calibration standard samples can be mixtures and pure phases. Relative calibration constants must be established at calibration standard samples, which are mixtures of two or more phases (that means 'pure standards', having C_i = 100% are not acceptable). Each sample must contain the internal standard phase if the Internal standard model is to be used. If the Matrix flushing model is to be used, then the best (highest) precision of the (relative) calibration constants can be obtained if each standard sample does contain the reference phase.

For (thin) calibration standard samples for mass determination, the mass of the analytical phases in each sample should be known.

11.3.5 MASS ABSORPTION COEFFICIENT, MAC

The mass absorption (or attenuation) coefficient of the sample can be accounted for in four essentially different ways, by choosing different calculation models in the analysis programs. The model chosen depends on what you know about the sample.

For infinitely thick samples:

- If the mass absorption coefficient of the samples is precisely known, then you can use the General model with absolute calibration constants and enter the value of MAC (in cm^2/g). In practice this will only be possible if you have a way to measure the MAC, for example by measuring the absorption of thin samples in transmission, or by using the Compton scattered radiation.

NOTE: For calculation of Mass Absorption Coefficients of compounds and mixtures, you can use the "CALCULATOR, Mass absorption" command in the UTILITIES program (refer to Chapter 13.2.2).

- If you know that the mass absorption coefficient of the samples is constant (for example in the case of phases with the same chemical formula, like TiO2: Rutile and Anatase), you may use the Straight line model with its own calibration constants:

$$C_i = B_i \times I_i$$

- The same method may also be used if the mass absorption coefficients of the compounds are not equal but if all samples will have very narrow concentration ranges for the components. In this case we may assume the small parts of the 'calibration curves' that we use to be straight.

- If you do not know the MAC of the sample and if the concentration ranges are large, then you have to use a method of internal intensity ratio and relative calibration constants. There are two different approaches:

  a. You know the sum of the concentrations S (total of analytes), then you can use the Matrix flushing model, or the Binary model. The Binary model is the special case for two analytical phases.

     You have to choose one phase as the Reference material, for which the calibration constant is made 1.0.

     With the formula:

$$C_i = \frac{B_i \times I_i}{SUM(BxI)} \times S,$$

     the mass absorption coefficient is flushed out of the concentration formula. For the Binary model the formula is:

$$C_i = \frac{S}{1 + \frac{B_j}{B_i} \times \frac{I_j}{I_i}}$$

If you do not know the total of analytes then you can establish 'relative' weight fractions for the phases which are analysed.

  b. If you want to analyse one or more phases without knowing the other phases in a mixture, then you can add a known amount (C_s) of Internal standard material, for which the calibration constant is made 1.0. The formula is:

$$C_i = \frac{B_i}{B_s} \times \frac{I_i}{I_s} \times C_s,$$ also here MAC is eliminated.

The concentration of the internal standard (C_s) can be constant or different for all samples. The latter method is easier to use for precise 'weighing in'.

NOTE: For Internal standard material it is advisable to choose a material which is cheap and readily available, which has a constant composition and structure, and which has only a few, strong, non-overlapping lines. It should not give preferred orientation.

For thin samples:

- If you want to analyse concentrations, the above mentioned formulas can be used after thin sample intensity conversion. For the analysis of mass the transmission factor is included in the formula:

$$M_i = B_i m \times I_i \times \ln(\frac{1}{T}) = B_i m \times I_i m$$

11.3.6 ANALYSIS PROGRAMS, MODELS

In the Analysis program, type Quantitative, the analytical and overlapping phases are combined with the appropriate calculation model and information about the sample (MAC, total of analytes, concentration of Internal standard, and so on). It is used for calibration as well as for analysis of unknown samples. The calculation models are described in Chapter 11.3.5.

It is not necessary to use the same model or analysis program for calibration as well as for analysis. For the calibration of a phase which had not yet been calibrated an analysis program for only two phases (the reference and the new analytical phase, for example) can be used. For the analysis of the unknowns this phase can be combined with a number of previously calibrated phases in an analysis program. For the new phase even different overlap corrections can be used in the two analysis programs (the program used for calibration and the one for analysis).

The output of results will contain the figures of the counting statistical errors (Precision) for: gross intensity, corrected intensity, thin sample parameters and transmission factor, conversion factor, converted intensity, net intensity, calibration constant, concentration and mass. It is expressed as absolute precision (same units as concentration) for concentration and mass and as relative (%) errors (always 1 sigma).

11.3.7 CONCENTRATION, WEIGHT FRACTION, MASS

The weight fraction or concentration of the component of a mixture may be represented in two different ´units´ (it can be expressed in two different ways) in input and output: as percentage (%) or decimal fraction. You may choose one of these options with the commands:

Options/defaults, Representation (refer to Chapter 11.3.11).

Mass of an analytical phase is always expressed in milligrammes (mg).

11.3.8 EXTERNAL MONITOR

The intensity of an external monitor sample can be used to compensate for the instrumental intensity fluctuations. This is necessary if the general model or the straight line model for concentration calculation, or the thin sample on polycrystalline plate model for mass calculation is defined in an analysis program.

The monitor sample can be any stable and mechanically rigid sample, preferably with a high intensity peak. It should have good ´particle statistics´: it must be finely grained powder with minimum texture.

The analysis program defined for it will contain only one phase: the strongest peak. The phase that you assemble for the monitor can be a peak phase with maximum search, no background measurement (gross intensity only).

The measuring time at the top should be sufficient in order to have negligible counting statistical error. For example you might choose the time such that the gross counts are in the order of one million (10^6) counts. Note that the relative statistical error of the monitor measurement is added to the errors of the analytical phases of the ´unknown´ samples.

For the same reason of obtaining small statistical errors it is impossible in an External monitor program to use either constant background correction or line overlap correction. Gross counts will always have the same contribution of background and overlaps because we measure always the same sample, so there is no need for correction.

If you are going to use the monitor ratio method for one or more analysis program, you must measure the monitor sample before you do measurements on calibration standard samples or on analytical samples.

It is advised to measure the external monitor sample each day. If you always use the same file name then it will be easy to keep record of the condition of your instrument because the subsequent versions of the monitor QI file will contain the peak positions and intensities. For calculations the system will always take the highest version number; the most recent measurement results. This ´current monitor´ intensity Mc is stored in the user´s DEFAULTS.APD file, together with its precission (%), measurement date and time, and monitor version number.

If there is more than one diffractometer connected to the system, then you can use the same monitor sample and the same measurement parameters for the different diffractometers. It is advisable to use different file names for the different diffractometers because the history of each diffractometer is then easier to trace for you. For calculations the system takes always automatically the most recent monitor intensity Mc measured at the same instrument as the ´unknown´ sample you want to analyse; the proper monitor intensity is stored in the QI file of the sample (Mf).

The first time the phase file (APDPHA.DAT of the same diffractometer) is accessed again after the monitor has been measured, the system stores the value of Mc in the phase file as Mp: the (phase) ´Calibration monitor´ intensity. Mp is stored without precision, date, or time and will not be changed anymore.

For concentration calculation (general or straight line model) the monitor intensity ratio is applied as follows:

$$C_i = I_i \times B_i \times MAC \times \frac{Mp}{Mf} \quad \text{, in which:}$$

$$\frac{Mp}{Mf} = \text{´monitor ratio´}$$

In a thin sample mass calculation:

$$M_i = I_im \times B_im \times \frac{Mp}{Mf} \quad \text{, here:}$$

$$I_im = I_i \times \ln\left(\frac{1}{T}\right)$$

If the plate intensity reference is used for thin sample conversion:

$$T = \left(\frac{I_p}{I_p r} \right)^{\sin\theta p}$$

$$\frac{I_p}{I_p r} = \text{´plate intensity ratio´}$$

$$I_p r = I_p 0 \times \frac{Mf(QI)}{Mf(QP)} = \text{´related plate intensity}$$

$$\frac{Mf(QI)}{Mf(QP)} = \text{´monitor ratio´ for plate intensity}$$

QUANTITATIVE ANALYSIS 25-FEB-86 13:21

Quantitative data file: GM3.QI 28-JUN-85 12:00
Sample identification: G M3
Diffractometer system: 1

Phase number	Phase type	Phase angle	Gross intensity	Background intensity	Background correction	Corrected intensity	Prec (%)
20	Peak	25.640	612.1	68.9 73.7	72.5	539.6	0.6
21	Peak	26.700	2448.3	54.3	54.3	2394.0	0.2
22	Peak	52.575	802.6	38.9	38.9	763.7	0.5
23	Peak	54.910	184.4	53.7	53.7	130.7	1.6
24 P1	Peak	44.610	2833.4	37.6	37.6	2795.9	0.2

Analysis program 23: THIN SAMPLE ON AL Model: Thin sample (Mass)

Individual clean plate file:	GM3.QP				
Sample identification :	GM3 CLEAN PLATE				
Clean plate intensity :	637817.6	Prec (%):	0.0	24-JUN-85	13:17
QP file monitor intensity :	41538.5	Prec (%):	0.0	24-JUN-85	9:58
QI file monitor intensity :	41538.5	Prec (%):	0.0	24-JUN-85	9:58
Monitor ratio :	1.00000	Prec (%):	0.0		
Related plate intensity :	637817.6	Prec (%):	0.0		
Plate intensity ratio :	0.00438	Prec (%):	0.2		
Transmission factor :	0.12735	Prec (%):	0.1		
MAC * density * thickness :	1.03043	Prec (%):	0.0		

Phase number	Angle (deg)	Conversion factor	Prec (%)	Converted intensity	Prec (%)
20	25.640	1.00009	0.0	539.6	0.6
21	26.700	1.00013	0.0	2394.3	0.2
22	52.575	1.00962	0.0	771.0	0.5
23	54.910	1.01158	0.0	132.2	1.6

Phase number	Overlapping phase corr	Net intensity	Prec (%)	Mass rel intensity	Prec (%)	Calibration constant	Prec (%)
20	0.0	539.6	0.6	1112.1	0.7	0.1631E-01	0.6
21	0.0	2394.3	0.2	4934.2	0.3	0.1968E-02	2.9

QI file monitor intensity :	41538.5	Prec (%):	0.0	24-JUN-86	9:58
Calibration mon intensity :	44053.8				
Monitor ratio :	1.06055	Prec (%):	0.0		

Phase number	Mass (mg)	Precision (abs)	(%)	Phase name
20	19.2373	0.2591	1.3	CORUND (012)
21	10.2972	0.3374	3.3	QUARTZ (101)

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If a monitor measurement did not give correct results, the previous correct monitor situation can be restored. If you made an error, for example: you measured a wrong sample, or you measured the monitor but forgot to open the shutter or switch the x-rays on, an incorrect Mc value is stored. This situation can be rectified if you give the command "MONITOR, Restore current" in the program SYSTEM PREPARATION, CALIBRATION.

Should the external monitor sample be damaged, then you have to use another sample as the monitor. You do not have to recalibrate the system for the phases defined in the analysis programs in which a monitor ratio has been specified; instead you may use the command "MONITOR, New version" in the program SYSTEM PREPARATION, CALIBRATION.

11.3.9 CALCULATE

The CALCULATE command can be used for analyses using the Addition method, or for doing other quantitative analyses interactively; if applicable with alternative analysis programs.

11.3.9.1 Addition

The standard addition method can be used if a complete calibration procedure seems overdone or if it is impossible, for example if you want to analyse only one phase in one sample of which the further components are not important.

In this case you have chosen (in System preparation, Assemble Analysis program) the analytical phase and the reference phase. You measure the original sample with this analysis program, then add a known weight fraction of powder of the analytical phase (weigh and mix carefully) and measure the enriched sample with the same analysis program. You can repeat this procedure with the same or different weight fractions of analytical phase material for eliminating weighing, mixing and sample preparation errors.

For analysis, after the CALCULATE command you enter the filename of one of the samples, together with the additional concentration of the analytical phase in this sample. Then the system requests the second sample filename and additional concentration, this is repeated until you enter RETURN for the filename, or until 10 filenames have been entered.

The system checks whether you have entered more than 1 data file, if not, the message "Minimum two quantitative data files required" is displayed. Subsequently, the system checks whether you have entered at least one QI file with additional concentration = 0.0 (this does not need to be the first file entered).

If you have entered more than two data files the system will display a table of the 'enriched' samples (with additional concentration >0). The table shows for each of the enriched samples the result as if each sample had been used in a single addition: the concentration of the analytical phase in the original sample. You may check the spread in the results and consider whether you want to start again leaving out one or more of the samples (refer to figure 11.8).

The answer to the next question: "Plot? Yes, No:=" defines whether you want to have the results plotted on terminal or printer. On a plot you can see clearly how well the individual samples fit the curve. Each enriched sample is indicated in the plot by the entry sequence number. The original sample is always in the origin of the plot.

The "Additional concentration" A(%) of the analytical phase is the horizontal axis. The vertical axis is the "Additional relative intensity (ratio)" indicated in the following formulas:

Single addition

$$C_1 = \frac{R_1}{R_2 - R_1} \times A_2$$

Multiple addition

$$C_1 = \frac{A_i}{\frac{R_i}{R_1} - 1}$$

$R = \frac{I_a}{I_r}$, I_a = intensity of analytical phase
I_r = intensity of reference phase

A = additional concentration of analytical phase

i = sample measurement number: sample 1 = original sample (with A_1 = 0%).

$$\text{"Additional relative intensity"} = \frac{Ri}{R_1} \times 100\%$$

Finally the system displays the concentration or weight fraction of the analytical phase in the original sample calculated from all the samples used in the procedure. Linear regression is used in the case of multiple addition (more than two data files).

11.3

Alternative calculations

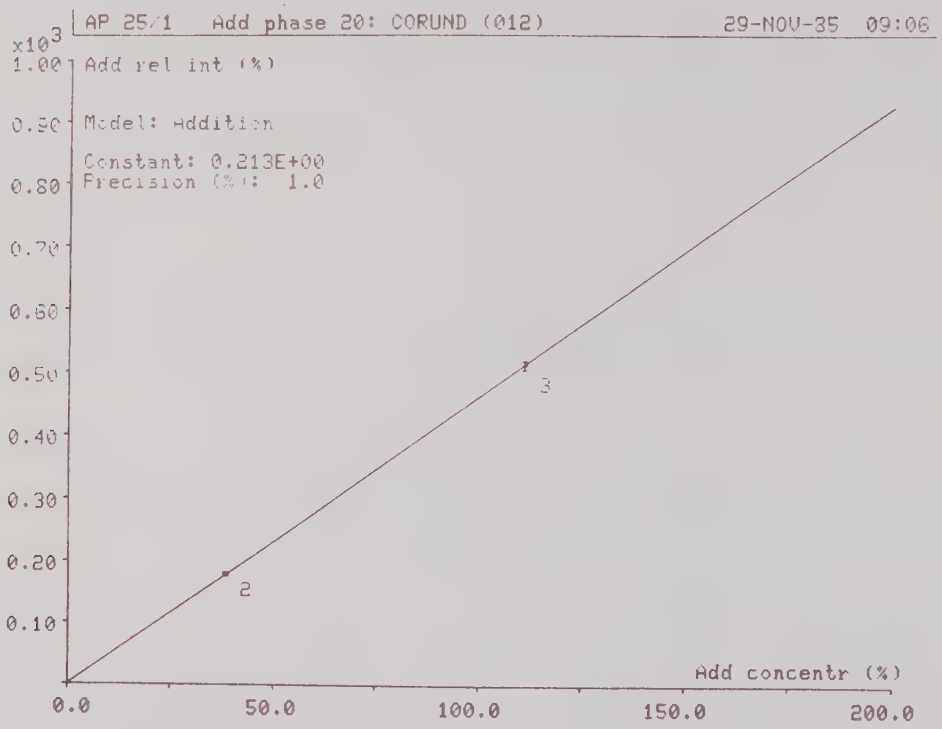
With the CALCULATE command it is also possible to perform an alternative calculation of concentrations or mass. The system will request a quantitative data file name (QI file), it presents the measurement results and the analysis program number with which it was measured. You have the possibility to choose another analysis program number for the calculation than was used for data collection. If you enter "?" instead of an analysis program number the system will display a ´map´ of the existing analysis programs for the same diffractometer. The results of the calculation will be sent to the printer, the terminal, or to a file, depending on your choice in Options/defaults.

```
Quantitative data file name  4 =  :=

QI file  Concentration   Precision
number       (%)        (abs)    (%)
-------------------------------------
   2         21.05        0.00     0.0
   3         21.30        0.00     0.0

Plot?  Yes, No = No := Y

Plot to: Terminal, Plotter = Terminal :=
```




```
Phase   Concentration   Precision        Phase
number       (%)        (abs)    (%)     name
-------------------------------------------------------
  20         21.23        0.21    1.0     CORUND (012)

CALCULATE, LIST, OPTIONS/DEFAULTS = CALCULATE :=
```

Figure 11.8 Standard Addition

11.3.10 LIST

With this program you can list QI files, Monitor values, and the different calibration constants. You may send the data to your terminal, the printer, or to an ASCII file, depending on what you define in Options/defaults.

Monitor

You can list the Current monitor values for the diffractometers in the system, or the Replacements. Current monitor values are the monitor intensities Mc for each diffractometer as stored in the Defaults file. They are listed with precision, measurement date and time, and the monitor version number. With the Replacements option the following data are listed for each diffractometer: monitor version numbers, ratios (ratio of New over Old monitor intensities), and replacement date (refer to Chapter 7.5.7).

NOTE: Do not list Monitor data while you are measuring the monitor sample as the new results might not be correctly stored.

```
QUANTITATIVE ANALYSIS                                    25-FEB-86  15:27
-------------------------------------------------------------------------

CALCULATE, LIST, OPTIONS/DEFAULTS = CALCULATE :=

Quantitative data file name = ZM2.QI :=


Quantitative data file: ZM2.QI    27-JUN-85  16:20
Sample  identification: Z M2
Diffractometer  system: 1

Analysis program number =  20 := 21


Analysis program  21: QUARTZ AND CORUNDUM   Model: Matrix flushing

Total of analytes (%) = 100.00 :=


Phase    Concentration   Precision       Phase
number       (%)        (abs)    (%)     name
-------------------------------------------------------------
  20 IS     41.71         3.68     8.8    CORUND (012)
  21        58.29        13.40    23.0    QUARTZ (101)

CALCULATE, LIST, OPTIONS/DEFAULTS = CALCULATE :=
```

11.3

Figure 11.9 Example of Calculate Quantitative Analysis

Calibration constants

You can list the calibration constants for each diffractometer in the system. You have to choose the type of calibration constants: General, Straight line, Mass, or Relative. For each phase is listed: phase number, calibration constant and its precision (%), calibration date and time, and the phase name.

11.3.11 OPTIONS/DEFAULTS

Default options can be chosen for Listings and Representation of units.

Listings

You may choose to have no output at all (only disc files will be written), short output, or full output during (automatic) analysis. Listings may be displayed on the printer, on your terminal, or they may be saved on an ASCII file. If you choose optional, the question will be asked at the proper time.

Representation

Concentrations can be represented in input and output as percentages or as (weight) fractions.

11.3.12 QUANTITATIVE ANALYSIS: STEP-BY-STEP

In this section you will find a detailed description of all the steps necessary for quantitative analysis of a number of phases. The main parts of the procedure are described in Chapter 11.3.1:

- System preparation: . Assemble Phases and Analysis program
  . Calibration

- Data collection and Analysis, normally combined in an Automatic Analysis Procedure following the Analysis program.

System Preparation

Assemble a goniometer scan, for example from 10 to $60^{o}2\theta$, but in special cases a lower starting angle (large d-values; clays, organics) or higher final angle (small d-values; metals, alloys) has to be used.

Then perform Data collection on a number (1 to 4) of representative calibration standard samples, preferably those samples that have the extreme concentrations of the compounds to be analysed. Pure compounds can be used as well. Use the Graphics Plot and Compare programs to determine which peak of a compound will be chosen as the Phase that represents the compound (criteria: high intensity, no -or smallest- overlap).

Plot over a small angle range with adapted Intensity scale, in these detailed graphs you can determine the exact positions for Peak and Background points, and of Starting and Final angles. With the "P" command the angle position of the cursor is displayed on the screen. Peak positions can of course also be read from the DI file after Pattern treatment, Peak search. These angle positions have to be used in Assemble, Phases.

If there is no free-standing peak for a compound then you can determine in the graph which is the overlapping compound, so that in Assemble Analysis program you can input the number of the Overlapping phase.

Assemble an analysis program (Quantitative) containing all phases of interest, Analytical as well as Overlapping, Internal standard and so on. In case of doubt whether there is an overlap problem, you could input more than one Phase for the same compound.

Do Data collection on maximum 25 calibration standard samples using the Analysis program just assembled for the calibration.

Use Calibration, Assemble calibration set to input the known Concentrations; give RETURN for the Net intensities as you will read these in from the QI files later (Input QI Files). The Analysis program number for the Calibration set need not to be the same as the one used for Data collection. In this way you can try out different Phases for the same compound or different Overlap corrections by assembling different Analysis programs and assembling Calibration sets for them.

NOTE: Overlap correction factors must be determined 'off-line'.

After the command Calibrate the calibration constants can be stored for each of the analytical phases of the analysis program. With the Plot command the 'calibration curve' for a phase will be displayed. This enables you to check the results for the different calibration standard samples, see whether there seem to be outliers. If there is such a sample deviating more than the others from the straight line, then you should first check whether this is the case because of non-correct background definition or overlap correction. This can be checked by making a small scan and a plot of the RD file (or by re-evaluating the original scan). If this seems to be correct, then see whether the sample has been prepared correctly (preferred orientation, for example). Of course it is also possible that the concentration which has been entered for the compound in this sample is not correct.

With the List QI file command the gross counts (number of counts accumulated during Data collection) for Peak, Area, and Background are displayed. This information can also be used to find problems, for example erroneous background points.

Data Collection and Analysis

After Calibration has been done, unknown samples can be measured and analysed by entering the appropriate analysis program number for Data collection.

If you want, it is also possible to use another analysis program for the same sample (QI file) after you have given the commands Analysis, Quantify, and Calculate.

A worked example of a complete sequence of quantitative analysis is given in Appendix D.

11.4 LINE PROFILE ANALYSIS

11.4.1 INTRODUCTION

Line profile analysis (LPA) is a technique to extract information on the microstructure (~ the imperfectness of the structure) of crystalline materials from the shape of x-ray diffraction line profiles. A comprehensive review can be found in the book by Klug and Alexander [1]; a review paper on LPA practice is [2]. A description of theory is given by Warren [3].

A line profile observed contains contributions from:

A. Structural imperfections such as finite crystallite size, lattice distortions (microstrains for example from mechanical deformation or concentration variations), stacking faults and microtwins, and so on.

B. 'Instrumental' effects by
   - the diffractometer used (slits, and so on)
   - the x-ray spectrum used (K-alpha doublet)
   - the sample used (surface roughness, absorption and so on)

It is usual to consider a line profile to be analysed (also denoted as h profile) as consisting of a combination of a structural profile (also denoted as f profile) and an instrumental profile (also denoted as g profile).

It is clear that you have to remove the contribution of the instrumental effects from the line profile to be analysed, before being able to evaluate the structural parameters.

The references (the number between square brackets) can be found in 11.4.5.

11.4.2 THEORY

The following paragraphs will describe:

1. How a line profile can be characterized mathematically.
2. How structural imperfections influence line broadening.
3. How the characteristic parameters of the structural profile are obtained from the profile to be analysed.
4. How the parameters characterizing the structural profile can be interpreted.

11.4.2.1 Mathematical Characterization of Profile Shapes

For the mathematical characterization of profile shapes two kinds of parameters are widely used:

- The Fourier coefficients, which allow a general and detailed description of line profiles.
- Breadth measures. These have limitations, for example: the asymmetry of a profile is not expressed by breadth measures.

Line profiles are usually recorded in practice as step scans. From these recordings the Fourier coefficients can be calculated.

$$A(n) = \frac{1}{a} \sum_{m=1}^{N} I(m) \cos \frac{2\pi nms}{a} \qquad (1a)$$

$$B(n) = \frac{1}{a} \sum_{m=1}^{N} I(m) \sin \frac{2\pi nms}{a} \qquad (1b)$$

in which: n is the harmonic number (n = 0,1,2,...N/2);

N is the number of intensity data I(m) of the profile in the step scan recording with sequence number m = 1,2,...,N;

s is the stepsize in 2θ or some function of θ (refer to Section 11.4.3.3);

a is the range over which the intensities I(m) are recorded (the 'period' for the Fourier transformation).

A(n) is usually referred to as a cosine Fourier coefficient and describes the symmetrical part of the profile.

B(n) is usually called a sine Fourier coefficient and describes the asymmetry.

From a line profile recorded as a step scan the halfwidth 2w (FWHM) can be estimated and also the integral breadth beta can be obtained: beta = peak area divided by the peak maximum (= the width of a rectangle with the same area and height as the peak concerned).

A profile, 2w, beta and its Fourier coefficients are shown in Figure 11.10.

11.4.2.2 The Influence of Structural Imperfections on Line Broadening

One way of discriminating between various line broadening effects is by looking at their dependence on the diffraction angle. The microstructural parameters calculated most frequently from line broadening are values for an average crystallite size and for a mean lattice distortion. If the integral breadth of an observed profile could be interpreted as only due to finite crystallite size, the volume averaged crystallite size D_v would be:

$$D_v = k.lambda/(beta.\cos \theta) \qquad (2)$$

This is the well-known Scherrer equation, where k is a constant with a value close to 1 but dependent on crystallite shape and hkl reflection, and lambda is the wavelength of the x-radiation used.

If the integral breadth of an observed profile could be interpreted as due to lattice distortions only, then an estimate for a mean lattice distortion e would be:

$$e = beta/(4 \tan \theta) \qquad (3)$$

From these formulas it will be clear that finite crystallite size and lattice distortions yield line broadenings with different dependencies on the diffraction angle 2θ. This provides a means of distinguishing between the two causes and for separating their effects if both effects occur simultaneously and this is usually the case in practice.

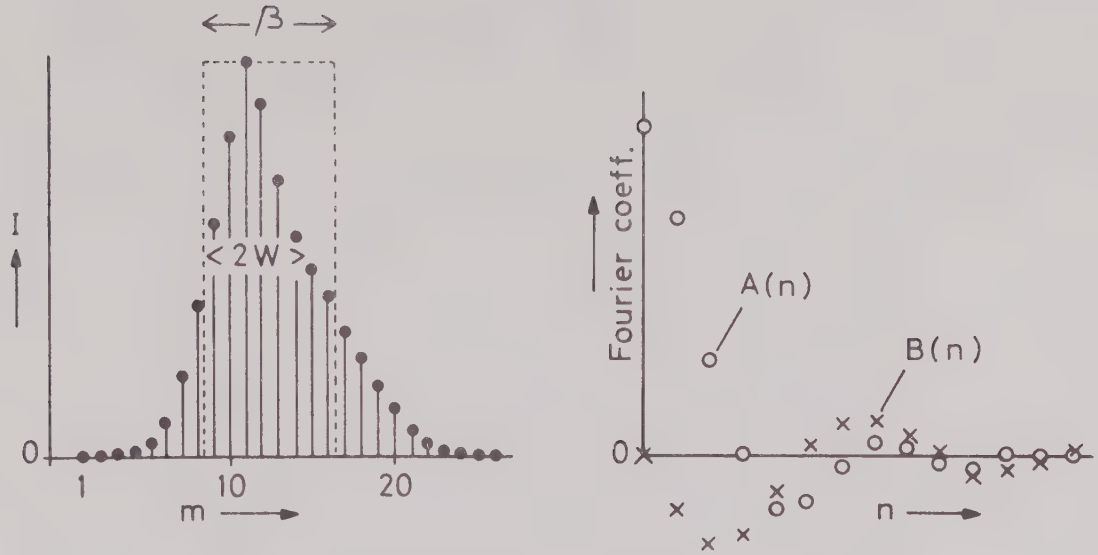


Figure 11.10 A line profile I(m) as a step scan recording with its half-width 2w and integral breadth beta and the cosine and sine Fourier coefficients A(n) and B(n) respectively.

Then - as well as in every other case in x-ray diffraction where two (or more) kinds of broadening effects occur simultaneously - the profile resulting from these broadenings is well-described by the convolution of these broadening functions. Convolution is a mathematical conception frequently used in optics and in diffraction (for example [1]) and it combines very nicely with the use of Fourier series.

11.4

11.4.2.3 Obtaining Characteristic Parameters from the Profile

Both the g and h profiles should be corrected for background and also for the Lorentz-polarization factor (see for example [4]). The $alpha_2$ component of the K-alpha doublet should be stripped to obtain representative values for half-width and integral breadth. The $alpha_2$ stripping - according to Delhez and Mittemeijer [5] - may also be needed before performing the Stokes deconvolution discussed in the following paragraphs.

If you assume that the profile to be analysed h(x) is the convolution* of the structural profile f(y) and the profile g(z) describing the broadening due to instrumental effects, then the normalized Fourier coefficients of h(x) denoted with H(n) are simply obtained from:

$$H(n) = F(n) \cdot G(n) \qquad (4)$$

where F(n) and G(n) are the normalized Fourier coefficients of f(y) and g(z) respectively; n is the harmonic number**, H(n), F(n) and G(n) are complex numbers each of which can be expressed in cosine and sine Fourier coefficients (real and imaginary parts):

$$H(n) = A^H(n) + iB^H(n) \qquad (5a)$$
$$G(n) = A^G(n) + iB^G(n) \qquad (5b)$$
$$F(n) = A^F(n) + iB^F(n) \qquad (5c)$$

From equation (4) it is clear, that the Fourier coefficients F(n) of the structural profile f can be calculated easily by a division of complex numbers.

$$F(n) = H(n) \,/\, G(n) \qquad (6a)$$

Using (5a, b, c) you obtain:

$$A^F(n) = \frac{A^H(n)A^G(n) + B^H(n)B^G(n)}{A^G(n)^2 + B^G(n)^2}$$

$$B^F(n) = \frac{B^H(n)A^G(n) - A^H(n)B^G(n)}{A^G(n)^2 + B^G(n)^2}$$

For an explanation and the mathematics of convolution as used here you are referred to Warren [3]. Convolution is also called ´folding´ or ´fold´.

** *It is useful to replace the harmonic number by a (correlation) distance L in a crystal space. From basics of Fourier analysis it follows that incrementing n by 1 corresponds to an increase in L. If the profiles before Fourier transformation were on a 1/d (= 2 sin θ/lambda) type axis, then L = n/a (Angstrom!), where a is the range - translated to 1/d - over which the profiles were measured.*

This method of deconvolution or unfolding was originally introduced in x-ray diffraction by Stokes [6].

From $A^F(n)$ and $B^F(n)$ the structural profile f(y) can be synthesized, but this is impractible. Moreover $A^F(n)$ and $B^F(n)$ can be interpreted directly in terms of crystallite size and lattice strains (see paragraph 11.4.2.4).

It is advantageous to use the absolute values -or moduli- of the Fourier coefficients, the main reason being that the positions of the centroids of the profiles concerned become unimportant (refer to [2]):

$$|F(n)|^2 = A^F(n)^2 + B^F(n)^2 \qquad (7)$$

To obtain the halfwidth $2w^f$ and the integral breadth $beta^f$ of the f profile a method developed by Langford [7] can be used. This method assumes that all profiles f, g and h can be represented sufficiently accurately by Voigt profiles. A Voigt profile is the convolution of Cauchy functions (= Lorentzians) and gaussians (= error functions); these functions are frequently used in x-ray and neutron diffraction to describe line shapes.

Voigt profiles are symmetrical because the constituent profiles are so. Measured profiles are usually strongly asymmetrical because of the presence of the K-alpha doublet and therefore $alpha_2$ stripping is necessary here.

The shape of a Voigt function (not regarding the absolute intensity values) can be described with two parameters, for example: its halfwidth 2w and its integral breadth beta. From 2w and beta for each of the g and h profiles the integral breadths $beta_c$ and $beta_g$ of the Cauchy and gaussian components can be obtained using a calibration graph or empirical equations [8]:

$$beta_c/beta = 2.0207 - 0.4803(2w/beta) - 1.7756(2w/beta)^2 \qquad (8a)$$

$$beta_g/beta = 0.6420 + 1.4187\{(2w/beta)-2/pi\}^{1/2} - 2.2043(2w/beta) + 1.8706(2w/beta)^2 \qquad (8b)$$

Then the integral breadth of the Cauchy part of the Voigt function describing the f profile can be obtained from:

$$\text{beta}_c^f = \text{beta}_c^h - \text{beta}_c^g \qquad (9a)$$

and the integral breadth of the gaussian part from:

$$(\text{beta}_g^f)^2 = (\text{beta}_g^h)^2 - (\text{beta}_g^g)^2 \qquad (9b)$$

An example of this method including the subsequent size - strain determination is given in [2].

Alternatively beta_c^f and beta_g^f can be estimated from the Fourier coefficients of the f profile calculated using Stokes' deconvolution method as previously described. The Fourier transform of a Voigt function is:

$$F(n) = A_o \exp\,[-2\,\text{beta}_c^f\, n - \text{pi}\,(\text{beta}_g^f)^2\, n^2] \qquad (10)$$

where A_o is a constant and therefore values for beta_g^f and beta_c^f can be obtained by matching a parabola to the natural logarithm of a number of subsequent $A^F(n)$ or $|F(n)|$ values. This method has the advantage that no errors in beta_c^f and beta_g^f can arise from the deconvolution itself, since the Stokes deconvolution uses no assumptions on the shape of the g and h profiles, whereas the Langford method assumes that both the g and h profiles can be described by Voigt functions.

The procedure using the matching of a parabola has the disadvantage that it is difficult to say how well the Voigt function estimated matches the structural profile f. Therefore both methods should be used with care and the numerical results should be examined critically. Yet for comparing analogous samples these methods are very useful.

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It should be noted that the total integral breadth of the f profile beta^f can be obtained from a calibration graph or from the empirical equation:

$$\text{beta}_g^f/\text{beta}^f = -b/2 + 0.5(b^2+4)^{1/2} - 0.132\ b \exp(-1.228\ b) \qquad (11)$$

$$\text{with } b = \text{beta}_c^f/\text{beta}_g^f$$

11.4.2.4 Methods for the Interpretation of the Parameters Characterizing the Structural Profile f

The interpretation of the parameters characterizing the structural profile f consists of:

1. Splitting of these parameters (breadth measures; Fourier coefficients) into contributions of finite crystallite size and lattice distortions. This splitting can be based on (i) knowledge of the θ dependence of both effects or (ii) assumptions concerning the shape of the profiles resulting from both effects.

   For (i) more than one f profile is required: a multiple-line method, whereas for (ii) only one f profile is needed: a single-line method.

2. The calculation of a crystallite dimension and a lattice strain from the separated contributions.

The following paragraphs describe the single-line and multiple-line methods used in the APD1700 Line Profile module (PW1864).

11.4.2.4.1 Single-Line Methods

It has become clear from practical experience that:

1. Finite crystallite size often yields a profile resembling a Cauchy function.
2. Lattice distortions often yield an approximately gaussian shaped profile.

This implies that the f profile resulting from both effects can then be described by a Voigt function.

(a) The Approximate Method

The approximate method is based on the assumption that all profiles concerned can be described by a Voigt function. It uses only the half-widths and the integral breadths of these profiles and it therefore does not use the full shape of the profiles measured and it neglects the asymmetry (nearly always present) in all profiles.

Using Langford's Voigt deconvolution method [7] (equations 8a and b) you obtain simply $beta_c^f$ and $beta_g^f$ (equations 9a and b). These integral breadth components can be interpreted in terms of an average crystallite size and lattice deformation [8] by substituting $beta_c^f$ for beta in equation (2) and $beta_g^f$ in equation (3).

If it is known that no lattice deformation is present or that crystallites are very large, then you should interpret the total integral breadth of the f profile $beta^f$ (from equation 10 and $beta_c^f$ and $beta_g^f$) as crystallite size or lattice deformation only using equation (2) or (3) respectively.

(b) The Fourier Single-Line Method

The Fourier single-line method is based on the assumption that only the f profile can be described sufficiently accurately by a Voigt function. In this case, only the asymmetry in the f profile is not accounted for accurately: asymmetries present in both the g and h profiles are eliminated since the Stokes' Fourier deconvolution method is used to obtain the Fourier coefficients of the f profile. As stated above equation (11) the interpretation of the moduli of the Fourier coefficients or the cosine Fourier coefficients is performed by matching a parabola to the natural logarithm of these Fourier coefficients. This yields an estimate for the zeroth (the very first) Fourier coefficient and for $beta_c^f$ and $beta_g^f$, which can be interpreted as in case (a).

11.4.2.4.2 The Multiple-Line Analysis

The dependence of the contributions of finite crystallite size and lattice distortions on diffraction angle (or spacing, or order of the reflection) is used in the APD1700 Line Profile module in the so-called Warren-Averbach analysis [3] which is the most detailed multiple-line method for size-strain analysis known at present. For this analysis two (or more) orders of the same hkl reflection are required, because only then are the same crystallites examined in the same direction. If it is known that the crystallites of the sample are (sufficiently) spherical and elastically isotropic, then different hkl reflections may also be used.

The Warren-Averbach analysis interpretes Fourier coefficients and the analysis can be applied to the cosine Fourier coefficients or to the moduli of the Fourier coefficients (equation (7)). The use of the moduli has advantages [2]. The APD1700 Line Profile module uses a modification by Delhez and Mittemeijer [9] of the original analysis, which is applied to two (orders of a) reflection(s) only.

The moduli of the Fourier coefficients or the cosine coefficients - denoted here by $A(L,d_1)$ and $A(L,d_2)$ with d_1 and d_2 the spacings belonging to the reflections concerned - are first normalized such, that $A(0,d_1) = A(0,d_2) = 1$*. Then these normalized coefficients are split into a so-called size Fourier coefficient $A^S(L)$, which is independent of d, and a mean squared strain $\langle eps(L)^2 \rangle$ [3,9]:

$$A^S(L) = \{d_1^2 A(L,d_1) - d_2^2 A(L,d_2)\} / (d_1^2 - d_2^2) \qquad (12)$$

$$\langle eps(L)^2 \rangle = d_1^2 d_2^2 / (2\pi^2 L^2) \cdot \{A(L,d_1) - A(L,d_2)\} / \{d_1^2 A(L,d_1) - d_2^2 A(L,d_2)\} \qquad (13)$$

* *L, the correlation distance in crystal space, is used here instead of the harmonic number n, see the second footnote in paragraph 11.4.2.3.*

Applying these formulas for all $A(L,d_1)$ and $A(L,d_2)$ pairs-at-the-same-L-value you obtain two curves (Figure 11.11) which are the complete results of the Warren-Averbach analysis. In practice it is convenient to deduce a few characteristic values from these curves. From the $A^S(L)$ curve you obtain D_{eff} a mean effective crystallite size (an area-weighted average) by determining the slope of the curve at L=0 and taking its reciprocal value. In this case, illustrated in figure 11.12.

D_{eff} equals the value of L cut from the L axis by the tangent to the $A^S(L)$ curve at L=0. The mean square strain is characterized by its value at $D_{eff}/2$ (50Å or 100Å are also usual values) as shown in figure 11.12. This simple procedure is usually complicated by the presence of a so-called 'hook' in the $A^S(L)$ curve:

If such a 'hook' is present, the tangent to the $A^S(L)$ curve at L=0 would yield too large a value for D_{eff}. A hook may have a physical origin [10, 11] and/or it may originate from the non-ideality of the measurement. In the latter case it is usually caused by an erroneous choice of the background and/or by a too short measuring range (truncation) in one or more of the four (= two pairs g and h) profiles used and you may try to improve the backgrounds chosen. In both cases a better estimate of D_{eff} is the reciprocal of the absolute value of the slope of the (more or less) linear part of the $A^S(L)$ curve (see figure 11.13), the program displays that estimate.

If it is assumed that the hook observed is caused by erroneous background choices, the $A^S(L)$ values should be corrected. Since an erroneous background yields an error in A(0,d) mainly, you should adjust $A(0,d_1)$ and/or $A(0,d_2)$ such, that the hook in the $A^S(L)$ curve disappears (see note 1). Usually this is done by linearizing the beginning of the $A(L,d_1)$ and $A(L,d_2)$ curves in the L range where the hook in the $A^S(L)$ curve exists.

NOTE 1: Obviously this procedure is incorrect if the hook has a physical origin, but there is no way to distinguish between the causes of the hook observed.

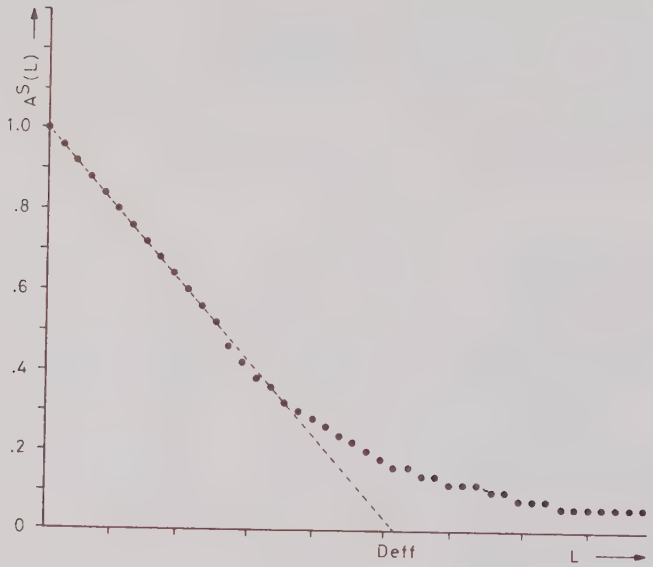

Figure 11.11 Plot of the results of a Warren-Averbach analysis

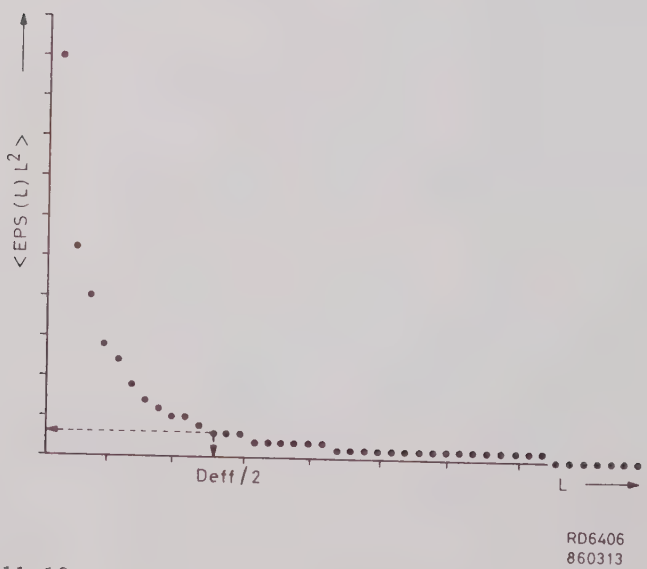

Figure 11.12 Second Plot of the results of a Warren-Averbach analysis

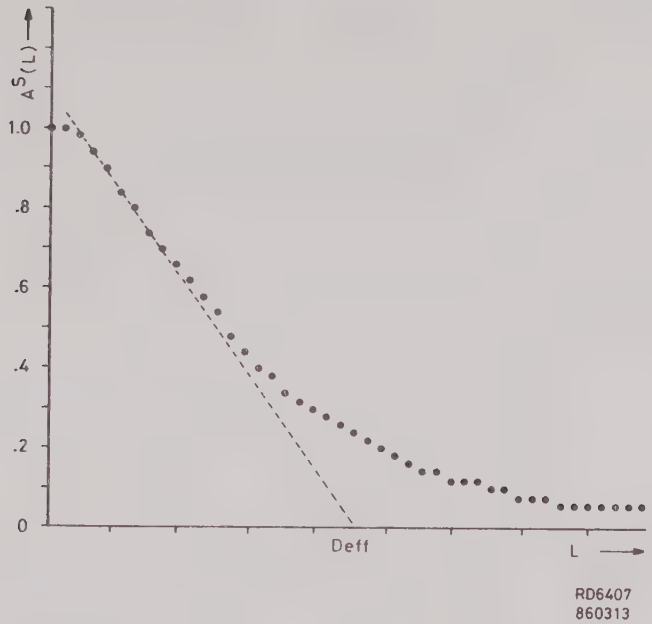

Figure 11.13 The ´hook´ effect in the $A^S(L)$ curve

11.4.3 PRACTICAL USE OF THE APD1700 LINE PROFILE ANALYSIS PROGRAM

11.4.3.1 Introduction

To perform a size-strain analysis two profiles are required (at least):

1. The "Analysed Profile" denoted "h" recorded from the sample to be investigated.
2. The "Profile of Standard" denoted "g" recorded from a reference sample which does not show finite crystallite size and/or lattice distortions. The main requirement is that the lattice spacing used for both the h and g profiles do not differ by more than about 2%. Also the linear absorption coefficient of both samples should not be too different.

The measurements should have a reasonable accuracy: preferably > 10000 counts net for the peak maxima and they should be recorded with appropriate stepsize (approximately 20 data points on the halfwidth of the K-alpha$_1$ profile) and with long tails: the measuring range should preferably be much larger than 10 times the halfwidth in order to reduce truncation effects.

The Profile of Standard "g" serves to be able to eliminate the broadening due to the diffractometer (for example: caused by slits) and the x-ray spectrum used (for example: the K-alpha doublet).

The program consists of three stages:

1. Corrections
   - Interactive parameter initialization
   - Elimination of background (linear, parabolic, or the best of these)
   - Correction for the angle dependence of the Lorentz-polarization factor, also if a diffracted beam monochromator is present [4]
   - Alpha$_2$ stripping [5]

- Determination of peak position, centroid, halfwidth 2w, integral breadth (beta), peak area. This step is executed twice: first for the g profile and secondly for the h profile.

2. Deconvolution this means the elimination of the broadening by the instrument and the x-ray spectrum used.

   - Axis transformation from 2θ-axis to 2 sinθ/lambda-axis (boundary condition is that the integrated intensity remains the same in both systems).
   - Fast Fourier transformation of profiles (on 2 sinθ/lambda-axis) after adjusting the measuring ranges of the profiles to the same length by adding zero intensities (if necessary).
   - Stokes deconvolution [6]

3. Size-strain analysis. You can choose from 3 different analyses:

   a. An approximate analysis using breadth measures.

   b. A single-line analysis.

   c. A multiple-line analysis: the Warren-Averbach analysis.

   To help you become familiar with the program and with size-strain analyses, test files are supplied:

   - "Analysed profiles" LPTST1.RD and LPTST2.RD are respectively a low-angle profile and a high-angle profile, and STLOW.RD and STHIGH.RD are the associated "Profiles of Standard". Also the files containing Fourier coefficients deduced from these files (required as input for the Warren-Averbach analysis) are present: LPAFC1.FC and LPAFC2.FC.

11.4.3.2 Entering Data File Names and the CORRECTION Stage

11.4.3.2.1 Entering Data File Names

For files containing an "Analysed Profile" or a "Profile of Standard" any file name is acceptable -as far as is allowed within the operating system-. Usually the file type can be recognized by its extension, but the file type is also internally stored. Acceptable file types are:

Raw data files	(usually having extension RD which is also the default value if no extension is specified).
$Alpha_2$ stripped files	(usually having extension A2)
Smoothed files	(usually having extension SM)
Peak files	(usually having extension PK). This file type is not recommended because it is likely that the background was not defined accurately enough.

Files should contain only 1 scan.

Starting and ending angle of the profile are asked to enable the user to extract an isolated peak from a long scan.

Default and limiting values are the starting and ending 2θ values of the scan.

For performing a multiple-line analysis (for which two pairs of profiles are required) it is useful to create the RD files by executing a batch file for data collection. Such a batch file could contain two jobs:

Job 1 executes Analysis program "1" containing only Gonio scan "1": a step-scan from θ_1 to θ_2 with stepsize s_1 and counting time t_1.

Job 2 executes Analysis program "2" containing only Gonio scan "2": a step-scan from θ_3 to θ_4 with stepsize s_2 and counting time t_2.

11.4.3.2.2 The Printed Report

By default a "Complete" printed report of the analysis is suggested.

The "Complete" report is intended as a report for the analyst. It contains more details than the "Main results" report which could be handed to the analysts "customer".

11.4.3.2.3 Determination and Elimination of Background

The "Profile of Standard" is treated first, followed by the "Analysed Profile".

For the determination and elimination of background, by default a linear background is suggested.

If you enter:

- "N" (No background subtraction) no further dialogue on background subtraction follows.
- "L", "P", "O" or <return> (Linear, Parabolic or Optimal background) Then, the "number of background data" is asked:
  By default 1/20 of the number of intensity data of the profile with a minimum of 5 datapoints is suggested.
  Limits : 1 to half the number of intensity data of the profile.
- (Background parameters)
  By default, for "Profile of Standard" 0.0 is always suggested, and, for "Analysed Profile" the values just calculated for "Profile of Standard"
  Limits : None.

Background elimination is not always necessary, for example: if peak files (usually filename extension PK) are used, but it is usually inevitable. Therefore it is recommended and proposed by the system to subtract a linear background interpolated between low and high angle end regions of the profile.

As an alternative a valley-type parabola can also be interpolated between the end regions. (This may be useful if the tail of a neighbouring profile is present).

When "optimal" is entered, the program determines whether a parabolic or a linear background matches the specified end regions best.

Another alternative is "Background parameters" where it is possible to specify the parameters of the background "parabola":

$$\text{Background counts} = A + BX + CX^2.$$

Of course, if a linear background seems preferable C is taken = 0.0. This alternative is useful, if the background is known from previous experiments. A good example is the case where the "Standard sample" is a well-crystallized strain-free copy of the sample analysed. Therefore the program proposes A, B and C of the "Profile of Standard" for the "Analysed Profile". To accept these default values you should have measured both profiles with the same divergence and detector slits and the same x-ray tube data (anode, kV, mA). Counting time differences are corrected for by the program.

If you specify Linear, Parabolic or Optimal background, the system asks for the length of the regions at the start and the end of the profile to match the background to. To find the best values for these regions it is advised to plot the profiles using the plotting routines in the Graphics program: display the profiles on the square root scale to observe the tails optimally.

11.4.3.2.4 Correction for the Angle Dependence of the Lorentz-polarization Factor

The Lorentz-polarization factor formulas available are characterized by CODE numbers:

Limits : 1 to 5

The system proposes the number appropriate in the current case according to rules given in the literature [4]. The relation between code number and formula will be shown if a "?" is given instead of a number. The system will automatically allow for the presence of a monochromator if one is fitted.

See Note 1 in 11.4.4 for further information.

11.4.3.2.5 $Alpha_2$ Stripping

$Alpha_2$ stripping uses two parameters:

a. The intensity ratio of the lines of the K-alpha doublet. If no monochromator is present this ratio is very close to 0.500. For accurate work if a monochromator is present, the ratio should be calculated (by hand) from a high angle profile (preferably 120 - 140° 2θ).
0.500 is suggested as default.

   Limits: 0.0 to 100.0

b. A correction to the angular distance DELTA between the lines of the K-alpha doublet as calculated using Bragg's law. This correction may markedly improve the result of the $alpha_2$ stripping, but it is in fact a fiddle factor which does not usually influence size-strain results appreciably. Therefore the program proposes 0.0 for this.

   Limits : DELTA + step size to 1/4 2θ range.
   Where DELTA is the distance in 2θ between the lines of the K-alpha doublet calculated using Bragg's law.

11.4.3.2.6 Determination of Peak Position, Halfwidth and Integral Breadth

To find the peak position a parabola, a gaussian and a Cauchy function (= Lorentzian) are matched to the top part of the profile. The top part can consist of the data points with intensities larger than 0.5, 0.7, or 0.85 times the highest corrected intensity (with a minimum of 5 data) whichever yields the best fit per point. So for each function firstly the best top part is determined and then the function yielding the best match is determined. This is called the "Optimal match".

Default : Optimal match.
(Optimal = best of Parabola, gaussian and Cauchy)
(No top & width: not accepted for Approximate analysis)

To determine the halfwidth (FWHM) the same functions are used to find the 2θ values at half the maximum intensity just calculated.

The peak position calculated is also used to determine the asymmetry of the profile. The program calculates the asymmetries of the halfwidth and the integral breadth. Asymmetry is the low-angle part of the width divided by the high-angle part with respect to the peak position.

A report "Data and results" of the CORRECTION stage is then given. The same report is printed when "Complete" printed report had been previously selected.

11.4.3.3 The DECONVOLUTION Stage

The deconvolution stage starts immediately after display of the "Data and results" of the CORRECTION stage. In this stage the following steps are done:

The Step-size on the 1/d axis. 2θ scales of the Analysed Profile and the Profile of Standard are converted to 2 sin θ/lambda (= 1/d) scales with the same step size. Since the conversion is a non-linear operation, a (linear) interpolation is needed to make them equidistant as required for the Fourier transformation.

The Fourier transformation of both sets of intensity data. The 1/d scale converts to the so-called L scale, which represents a distance in the crystallites perpendicular to the reflecting lattice planes (refer to 11.4.2.3 second footnote).

The Display of the Results of Deconvolution. The deconvolution is according to Stokes [6]. Displaying, printing and storing on disc file (file name is the same as that of the Analysed profile, extension FC) of the Fourier coefficients.

It is common and good practice to accept the defaults suggested by the program.

The results of the deconvolution stage can be displayed and printed in the "Complete" printed report when requested, but not in the "Main results" report.

For the plotting of the Fourier coefficients calculated, the length of the L axis to be displayed is suggested. This value can be increased or decreased after displaying the Fourier coefficients of the Structural Profile (f) the Analysed profile (h) or the Profile of Standard (g). After a change of the length of the L axis to be displayed the program proposes to display the Fourier coefficients of the f profile again, followed by those of h and of g. The meaning of the symbols in the plots are explained at the end of the plot.

After inspection of the Fourier coefficients obtained they can be displayed numerically on the terminal, printed in the report, or written to disc file (file name identical to that of the Analysed Profile with extension FC).

NOTE 1: A Single-line analysis should be performed after plotting the Fourier coefficients and before the printing and storing on disc file to help the user decide whether he wants a disc file or not. Such an FC file can be used for Single-line analysis.

NOTE 2: Writing the Fourier coefficients to disc file is obligatory if you want to perform a Multiple-line (Warren-Averbach) analysis. In that case, two of these files are required.

11.4.3.4 The APPROXIMATE Analysis

The analysis starts by entering raw data file names for the "Analysed Profile" and the "Profile of Standard" and performing the CORRECTION stage (refer to 11.4.3.2).

This analysis has no separate deconvolution stage since it is incorporated in the analysis itself. Therefore the results of the Approximate analysis follow immediately after the report of the CORRECTION stage.

A mean effective crystallite size and a mean relative strain are given. For convenience and for cases where the assumptions mentioned in 11.4.2.4.1 do not hold, an interpretation of the total integral breadth of the structural broadening is given using formulas 2 and 3 as given in 11.4.2.2.

NOTE: You should be careful when comparing crystallite size and lattice strain values from different types of analyses (see 11.4.4 Note 2).

11.4.3.5 The SINGLE-LINE Analysis

The Single-line analysis can be applied to:

(a) Fourier coefficients obtained in the course of a Single-line analysis starting from raw data files, or
(b) Fourier coefficients already stored in a file. Such a file must have been produced during execution of a Single-line or Multiple-line (= Warren-Averbach) analysis starting from raw data files.

The Fourier coefficient files have the extension FC and are written in ASCII so that they can be edited and printed without the use of special listing routines.

The program asks:

"Are Fourier coefficients to be analysed already calculated? Yes/No =:".

If you enter "No" the same dialogue for the CORRECTION stage as in the Approximate analysis (see above) follows. Then the DECONVOLUTION stage starts, and then after that the Single-line analysis.

If you enter "Yes" the name of the FC file is asked (FC is added automatically if no extension is entered). After entering an acceptable file name the main identification of the file is displayed as a check.

Then the question about the printed report is posed again (refer to 11.4.3.2.2).

The program then displays "the low L limit for Voigt matching" which can then be altered.

The Single-line analysis matches the Fourier transform of a Voigt function to a part of the Fourier coefficients obtained by DECONVOLUTION. The matching of the Voigt function is applied over a restricted range of the abscissa: the L axis (L is a distance in reciprocal space perpendicular to the reflecting lattice planes). This range is specified by the user, as well as the highest L value to be displayed when plotting.

The program then displays "Use |F|? Yes/No :="

The analysis can be applied to the moduli of the Fourier coefficients |F| and/or to the cosine Fourier coefficients; |F| has to be preferred (see 11.4.2.3 equation at (7)).

The program then displays "Automatic analysis or User specified mode :="

The analysis can be performed in Automatic mode or in User specified mode. The Automatic mode can only be chosen when you start the analysis!

In the Automatic mode the program searches the longest two L ranges (within the limits specified by the user -if possible-): one with the smallest average relative difference and one with the smallest difference of the values at L = 0 between the "measured" Fourier coefficients and the transform of the Voigt function matched.

These two solutions are displayed and it is stated which solution is marked as the best solution. The best of these solutions is the one with the smallest difference between values at L = 0, if the average relative difference is more than 1/5 that of smallest difference. This best solution can be plotted.

After this plotting (and replotting on printer if desired) you can specify ranges for Voigt matching (for example: the other solution found in the Automatic matching mode).

You can stop Single-line analysis of |F| by not changing the L limits. It is also possible to enter "/" to stop further analysis. If you do, the program proposes to perform a Single-line analysis on the cosine Fourier coefficients. Usually this will not be done, since the Moduli are better suited for size-strain analysis.

If no Fourier transform of a Voigt function could be matched, the program tries the Fourier transform of a Cauchy function. If a Cauchy function was matched, no strain value is given.

NOTE 1: If "ERROR 6 in subroutine LSQPAR" appears during execution of a single-line analysis, this does not invalidate the results. It should be regarded as a warning, and it will dissappear if you lower the high-L limit of the matching range sufficiently.

NOTE 2: Be careful when comparing crystallite size and lattice strain values from different types of analyses. (Refer to 11.4.4 Note 2).

11.4.3.6 The MULTIPLE-LINE Analysis (Warren-Averbach Analysis)

11.4.3.6.1 Starting the Analysis

The Multiple-line analysis can only be applied to FC files containing Fourier coefficients. Two files are required. If these files do not exist, they should be created by executing the stages CORRECTION and DECONVOLUTION for two Analysed Profiles (of the same sample measured with the same diffractometer parameters) using appropriate Profiles of Standard.

The two Analysed Profiles should be different orders of the same {hkl} reflections, although different reflections are also accepted if their spacings differ more than 10% (a smaller difference yields too large uncertainties in the results).

When entering the routine the first menu suggests to "Start new analysis", this should be accepted. Then the names of the files containing the Fourier coefficients must be entered. If no extension is specified the program assumes FC and checks if these files can be used. If yes, then it displays the main characteristics as a check, and displays again the main menu, now proposing to "Obtain size and strain" (= execute the Warren-Averbach analysis). As a rule it is advisable to accept this proposition even if it is known that a hook effect is present, because the program calculates lower limits for the Fourier coefficients at L = 0 for both profiles to correct the hook.

11.4.3.6.2 The Results

After the message "Warren-Averbach analysis has been executed", the size Fourier coefficients $A^S(L)$ can be displayed on the terminal or the printer as well as the mean square strain $\langle eps(L)^2 \rangle$. The number of data displayed in both plots can be changed after the questions "Plot the crystallite size FC ?" and "Plot the mean square strain ?" have been answered (with "T", "P" or "N").

When the $A^S(L)$ and $\langle eps(L)^2 \rangle$ values have been inspected, the same number of data can be displayed numerically on the terminal or the printer.

An estimate of the crystallite size D_{eff} (= mean effective column length) is given together with the mean square strain value at L = Deff/2 $\langle eps(Deff/2)^2 \rangle$.

The error estimate in D_{eff} is determined from the standard deviation of the slope of the $A^S(L)$ curve. Since $A^S(L)$ curves are often very straight for $A^S(L) > 0.5$ the standard deviation of the slope can be very small. Because of counting statistics, errors in background estimation, and so on, it is very unlikely that the relative error in the slope is < 1%: this condition sets a lower limit to the error displayed.

The errors in $\langle eps(L)^2 \rangle$ and its square root are calculated using the error estimate in D_{eff}.

11.4.3.6.3 Correcting the ´Hook´ Effect

For some explanation about the ´hook´ effect refer to 11.4.2.4.3.

After accepting the suggestion to correct the ´hook´ effect, you are asked if you want to use the "Cosine" or the "Moduli of the Fourier coefficients". Since the Moduli have advantages, it is usual to enter "M".

It is only in the crystallite size Fourier coefficients $A^S(L)$ that a ´hook´ is not allowed (although exceptions exist). Because of a ´hook´ effect $\langle eps(L)^2 \rangle$ can become negative at low L values which is physically impossible. These effects can be eliminated by adjusting the "measured" Fourier coefficients of both profiles at L = 0. These coefficients influence all $A^S(L)$ and $\langle eps(L)^2 \rangle$ values. You can also correct other "measured" FC (by linear interpolation done by the program), but this influences only the $A^S(L)$ and $\langle eps(L)^2 \rangle$ in the corrected L value range.

Usually you need to set the ´measured´ normalized first Fourier coefficients at a value somewhat larger than 1, the one for the high angle profile usually being larger than that for the low angle profile. For accurate measurements of profiles (long measuring ranges, and reasonable counting statistics) for the low angle profile 1.00 up to 1.1 and for the high angle profile somewhat higher are usual values.

To see how strong the ´hook´ in the ´measured´ Fourier coefficients is, you can display them. You can also inspect the numerical values of the interpolated low-angle and high-angle profiles as displayed together with the $A^S(L)$ and $\langle eps(L)^2 \rangle$ values. The ´hook´ is usually small for the low-angle profile (denoted with 1 in the plot). The high angle profile (denoted with 2 in the plot) usually shows a stronger ´hook´.

After this display the program returns to the same menu and proposes to correct the ´hook´:

"Automatic "hook" correction"

If you choose "user specified "hook" correction" you will be asked to enter values for the first (normalized) FC as estimated (for example, from the plots just discussed) of the low angle profile, and of the high angle profile. You usually accept that the program corrects only that coefficient. The values chosen are displayed and then the display and/or printing of the $A^S(L)$ and $\langle eps(L)^2 \rangle$ is repeated.

NOTE: Be careful when comparing crystallite size and lattice strain values from different types of analyses. (Refer to 11.4.4 Note 2).

11.4.4 NOTES

1. The angle dependence of the Lorentz-polarization factor.

   The Lp factor is the product of the Lorentz factor and the polarization factor belonging to the actual experimental circumstances.

   In this program the correction for the angle dependence of the Lp factor is always applied to profiles measured on a 2θ axis.

   The default values suggested by the system are determined as follows:

   The Profile of Standard should not be corrected for the lower 2θ values (CODE = 5), but for higher 2θ values using formula 1 (CODE = 1). The transition from CODE = 5 to CODE = 1 is set at 100^o 2θ for the start of the 2θ range of the Analysed Profile.

   The Analysed Profile is also not corrected for the lower 2θ values (CODE = 5), but for the higher 2θ values formula 2 is usually the best choice (CODE = 2).

   Here it is assumed (1) that the instrumental broadening dominates the spectral broadening at the lower 2θ values, but not at the higher 2θ values, and (2) that the structural broadening is larger than the spectral broadening (refer to [4]).

   If the Profile of Standard and/or Analysed Profile are recorded from specimens that are (very much like) single crystals, then formula 3 (CODE = 3) should be used instead of formula 1 and formula 4 (CODE = 4) instead of formula 2.

Formula number (CODE)	Formula
1	$\frac{1 + POL \cdot \cos^2 2\theta}{\sin^2\theta \cdot \cos\theta}$
2	$\frac{1 + POL \cdot \cos^2 2\theta}{\sin^2\theta}$
3	$\frac{1 + POL \cdot \cos^2 2\theta}{\sin\theta \cdot \cos\theta}$
4	$\frac{1 + POL \cdot \cos^2 2\theta}{\sin\theta}$
5	No correction

Here POL describes the extra polarization owing to the use of a monochromator:

$$POL = \cos^2 2\theta_{mon}$$

where $2\theta_{mon}$ is the diffraction angle of the monochromator. If no monochromator was used POL = 1. Since the system knows if a (graphite) monochromator was used it selects the correct value automatically.

2. Comparison of values of crystallite size and mean lattice strain from different types of size-strain analyses (refer to [2]) using the same measurements is difficult because:

   (a) The parameters describing the structural broadening are obtained in mathematically different ways, for example: integral breadth values obtained in the Approximate analysis (directly from the profiles) and in the Single-line analysis (indirectly from Fourier coefficients).

   (b) Crystallite size values obtained from Approximate analysis and Single-line analysis (using breadth measures implicity or explicitly) may be two or more times larger than the mean crystallite size obtained by the Multiple-line method (= Warren-Averbach analysis).

   The latter method (b) yields a so-called area weighted value, whereas the other method (a) yields a so-called volume-weighted value. Therefore it may be interesting to compare both kinds of sizes.

   Comparing strain values obtained from Approximate or Single-line analysis with values obtained from the Multiple-line method is even more difficult. No rules can be given.

11.4.5 REFERENCES

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11.5 CRYSTALLOGRAPHY, REFINE

11.5.1 INTRODUCTION

REFINE is an interactive program designed to calculate precise lattice parameters of a known phase using a set of reflections and a good estimation of the expected lattice parameters.

The REFINE program can also be used to calibrate a set of reflection angles using an internal standard, to search what space groups are possible for the lattice, and to provide indices for the reflections.

The program was originally designed to be used to successively delete the reflections of known phases in the search for a minor phase.

11.5.2 THE REFINE PROCESS

The reflection angles as measured by an x-ray diffractometer are related to the cell structure and dimensions. For example: the reflection angles of a cubic lattice are given by:

$$\sin^2(\theta) = (\lambda^2/4) \cdot (h^2+k^2+l^2)/a^2 \quad \text{for } h,k,l >= 0 \qquad (1)$$

Where lambda is the wavelength and a is the length of the cubic axis.

Similar formulas can be derived for other lattices. Using these formulas, theoretical diffraction angles can be calculated. Measured reflections matching the calculated reflections within a specified error window are used to calculate those cell dimensions which minimize the difference between the measured and the calculated angles. This REFINEMENT is done with a step-by-step decreasing error window.

As a result of REFINE the hkl indices of the measured reflections that correspond with calculated reflections are also known. The hkl indices can be scanned for SYSTEMATIC EXTINCTIONS to determine the space group to which the lattice belongs.

A systematic error in the set of measured reflections may occur. This systematic error is related to the angle at which the reflection is measured. A commonly used function for the relative systematic error in d is:

$$\cot(\theta)\cos(\theta)$$

see International Tables, vol 2 (1972) page 223.

The relative error in $\sin^2(\theta)$ can therefore be described as:

$$f(\theta) = \cos 2(\theta) \cdot \sin(\theta)$$

In that case (1) becomes:

$$\sin^2(\theta) = (\lambda^2/4) \cdot (h^2+k^2+l^2)/a^2 + E \cdot f(\theta) \quad \text{for } h,k,l >= 0$$

Where f is the angle dependent error and E a factor denoting the weight of the systematic error. This systematic error also covers the sample specific systematic errors, so E must be calculated separately for each sample. REFINE offers the possibility to refine the lattice parameters only, or the lattice parameters and E simultaneously, or E only.

Refinement of extrapolation factor E only is used especially for correction of systematic deviations of calculated and observed reflections. If a known phase has been mixed as internal standard with the unknown, its dimensions are precisely known, and the extrapolation factor can be determined. Afterwards the diffraction pattern is shifted according to the extrapolation factor.

Refinement of lattice pararmeters and extrapolation factor E simultaneously, is done:

- To take systematic errors which are present in the lattice parameter set used as well as in the observed list of reflections into account.

The program offers the possibility to calculate the theoretical reflections caused by a lattice, to calculate the cell dimensions, starting from a known indexing of reflections and to index the measured reflections using the refined lattice parameters and extrapolation factors.

11.5.3 OVERVIEW OF THE PROGRAM

A description of the program is provided in this section. This is done by giving short comments on the questions, and the possible answers of the program.

NOTE: Whenever a reflection is referred to, only its 2θ angular value is meant. Its intensity is not regarded in the Refine procedure, although the relative intensities of the reflections are reported in the tables.

The Refine procedure starts by presenting:

"File, Calculated reflections, Dimensions, = F :="

"F" : Read a DI file on which refinement (or some other manipulation) can be done.

Give minimum and maximum 2θ (default values from DI file):
Min. = 10.000:=
Max. = 60.000:=

Refinement on many reflections is very time consuming and often gives bad results when the starting set of lattice parameters are inaccurate. Therefore, it is suggested: not to take in more than 20 reflections in the region between 10 and 60 degrees 2θ, for a first trial with REFINE . If this refinement is successful a second one over a larger 2θ region can be executed, starting with a smaller value for the final precision.

"C" : Calculate all reflections theoretically caused by a set of lattice parameters. A specification of the space group of the lattice and the range over which the reflections have to be calculated will be asked for.

The number of reflections that can be stored is limited to 200. If the message "** too many reflections" occurs, the list of reflections is incomplete. The problem can be solved by choosing a smaller range over which the reflections must be calculated.

"D" : Calculate cell dimensions using known reflections. The lattice type and the reflections plus their indices will be asked for.

The calculation starts when a slash is given instead of a reflection.

NOTE: The number of independent indexed reflections must be equal to or greater than the number of independent axes of the lattice.

In the case of an orthorhombic cell, the input given below is insufficient for three reasons:

Input: angle = 20.6, h = 0, k = 1, l = 3
angle = 41.8, h = 0, k = 2, l = 6

a. For each axis a, b, and c one independent hkl is needed: the number of reflections is insufficient.
b. For the a axis the h = 0 gives no information.
c. The hkl indices given are interdependent.

"Lattice : Code, Number, Short = S :="

"C" : The lattice is indicated by the space group symbol (=Code). The notation is according to International Tables for X-ray crystallography, vol I (Birmingham 1965).

Examples:
Space group code P21 means space group number 4,
Space group code P65 means space group number 170,
Space group code P213 means space group number 198,
Space group code P6422 means space group number 181,
Space group code P42/mnm means space group number 136,
Space group code R-3c means space group number 167.

Upper and lower case characters are acceptable, for example: Fd3m, FD3M, and fd3m are acceptable for space group number 227.

"N" : The space group number (as used in the International Tables) can be given.

"S" : A short description using the crystal system and the bravais type can be given.

The crystal can be described by:

TR for triclinic/anorthic
M for monoclinic
O for orthorhombic
TE for tetragonal
R for rhombohedral
H for hexagonal
C for cubic

The bravais type can be described by:

P for primitive
I for body centered
F for face centered
C for C-face centered
A for A-face centered
B for B-face centered
R for the Hexagonal-R Bravais type

Permissable combinations of crystal system and bravais type are:

```
Cub--:--P       Hex--:--P
     :--I            :--R    <---> Rhomb
     :--F

TEtr-:--P       Orth-:--P     Mon-:--P      TRicl-:--P
     :               :--I          :
     :--I            :--F          :--C
     :               :--C          :
     :--F            :--A          :--B
```

Sometimes additional information is required, for example:

"Unique axis (B, or C) = B :="
This is asked for if the lattice is monoclinic primitive and the unique axis cannot be retrieved from the space group code.

"Output hexagonal or rhombohedral indexed = H :="
This is asked for if the lattice is hexagonal-R or rhombohedral.
The indices refer to a hexagonal or rhombohedral crystal.

"Input hexagonal or rhombohedral cell co-ordinates = H :="
This is asked for if the lattice is hexagonal-R or rhombohedral.

Depending on the crystal system, different dimensions are asked for. The dimensions to be specified are listed below:

Crystal system	Dimensions to be specified
TRiclinic	a,b,c,alpha,beta,gamma
Orthorhombic	a,b,c
TEtragonal	a,c
Hexagonal.P	a,c
Cubic	a
Monoclinic, b axis unique	a,b,c,beta > 90°
Monoclinic, c axis unique	a,b,c,gamma > 90°
Hexagonal.R	a,c
Rhombohedral	a,alpha

"Extrapolation factor = 0.000000 :="

A known extrapolation factor can be entered and kept constant during the refinement of the lattice parameters.

The system will report the number of reflections read in and suggesting to use a minimum number of lines starting from number 1 in the DI file onwards. Less lines are suggested for a cubic lattice than for a triclinic lattice.

The program will provide a table of indexing of reflections using the lattice parameters input by the user.

"Number of iterations (0..9) = 5 :="

The number of iterations for the refinement must be in the range of 0 to 9. Zero iterations can be selected for an indexing of reflections of the current lattice parameters. For normal refinement procedures, 5 iteration steps are used.

"Final precision = 0.0500 :="

The maximum allowed difference between a measured and a calculated reflection is asked for. REFINE starts with a large error window, decreasing every refinement step, as follows:

If 5 iterations have been requested and the final precision is specified as .05 degrees, then the error window for the first refinement step = 5 x .05 = .25 degrees. The next refinement steps are performed with error windows of:

.2500/2 = .1250 degrees
.2500/3 = .0833 degrees
.2500/4 = .0625 degrees, and finally
.2500/5 = .0500 degrees, as specified.

If zero iterations is selected, the final precision on the indexing can be selected as 0.250 for high symmetry systems, and 0.100 for low symmetry systems.

"Calculation of extrapolation factor: Yes, No = N :="

- If the answer is yes the next question is:
  "Refine extrapolation factor only Yes, No = N :="
- If the answer is yes, the lattice parameters remain unchanged and the refinement is done on the extrapolation factor only.

At this point the refinement will start. The input parameters are displayed in a standard format:

Number of refinement steps; the error window used, the number of singly explained reflections, the number of more than once explained reflections, the lattice parameters, and if requested the extrapolation factor are displayed.

If the total number of single and double explained reflections is less than the number of independent axes, REFINE stops. If only the number of singly explained reflections is less, the error window is automatically decreased. If enough singly explained reflections are found, but the reflections are interdependent the message "** not enough independent reflections given" appears. When the refinement process runs correctly, the number of singly explained reflections should increase and the number of doubly explained reflections should decrease.

At the end, all the dimensions found by the refinement procedure are reported.

"Crystal, Refine, Proceed = P :="

"C" : If you want to specify a new crystal description on which to refine.

"R" : If you want to do another refinement.

"P" : If you want to proceed with the rest of the program, the system answers with:

"Index, Calculated Reflections, Systematic Extinctions, Remove Explained Reflections, List current reflections, Write current reflections, Angle Correct:"

11.5

"Index" - On the basis of calculated lattice parameters the reflections are (hkl) indexed. A report is presented showing observed and calculated reflections, relative intensities as from the DI list, the difference in 2θ, the extrapolation factor and the (hkl) indices.

The calculated reflections given are those that lie within the error window specified by "Final Precision".

"Calculate Reflections" - Give a list of all reflections caused by the lattice. For example this can be used to inspect the original Raw data file for peaks not detected by the peak hunting sub-program.

The number of reflections that can be stored is limited (maximum 200). If the message "** too many reflections" occurs, the list of reflections is incomplete. Incomplete in the sense that an arrangement of increasing complexity of the hkl indices is used rather than an arrangement of increasing 2θ value of the first 200 reflections. By choosing a smaller region (which contains less than 200 reflections) over which the reflections must be calculated is complete.

"Systematic Extinctions" - Search for possible space groups using missing lines as apparent systematic extinctions.

This is done by searching for systematic extinctions in the indexing as found by REFINE. The conditions under which reflections are apparently extinct are displayed. The space groups having exactly the same conditions, and the space groups having one or more of the conditions as found are displayed. This is done for two purposes:

- the conditions as found, might be non-systematic but coincidental extinctions.
- some conditions include others (for example 001 for 1=2, and 001 for 1=6n). Because the International Tables list only the sharpest condition (in this case 001 for 1=6n), exact matching of conditions will not occur.

In both cases you must draw your own conclusions.

"Remove explained reflections" - Delete all measured reflections that were matched with calculated reflections. At least one iteration step of refinement must have been done. This feature can be used for a step-by-step elimination of reflections from the diffractogram.

The resulting DI file can be written to disc for other data evaluation.

"List current reflections" - A list of the reflections that are used as input for the Refine program is given.

"Write current reflections" - The current DI list is written to disc. It must be given a new name.

"Angle correct" - The extrapolation factor previously determined can be used to correct the reflections read in from the DI file. If an internal standard was used (after indexing of the internal standard using Refine) the DI file can be corrected and the lines of the internal standard can be removed using the command "Remove explained reflections". Thus an error corrected set of reflections will remain.

The extrapolation factor is set to zero.

11.5.4 PRACTICAL ADVICE

The REFINE program needs high quality peak position data, data collection must therefore be accurate using parameters such as: stepsize 0.01, time per step 2 seconds, and the step scan mode. The Peak Search procedure can be optimized for such high quality data by setting the minimum significance to 1. It is recommended to use an Internal Standard to calculate an extrapolation factor to correct the DI file.

11.5.4.1 Introduction

The routine uses an estimated set of lattice parameters as input, this set needs to be quite accurate. The space group number or code should be as described in the latest edition of Crystal Data Determinative Tables (U.S. Department of Commerce) Library of Congress Catalog card number 77-187758.

11.5.4.2 The Set-up

The first step of the program is to provide a table of Indexing of Reflections using the measured DI file with the lattice parameter set given by you, and a Final Precision of 0.05. The criteria to use to judge the table are:

1. Are the hkl indices simple (100, 110, and so on).
2. Are the values in the column "Difference 2theta" small and random.
3. Are the number of lines explained half or more than the number of lines used for the indexing?

NOTE: This automatic Indexing is comparable to a refinement using zero iteration steps. The value for the final precision is default 0.05. If the table contains very few or no lines, use a final precision value of 0.250.

To facilitate judgement, a calculation of the reflections for the set of lattice parameters has to be done. It is then possible to see whether the first line is measured, and what are the criteria for data reduction. The DI file can then be reduced to K-alpha$_1$ reflections only, and reflections of sufficient intensity. The reduced DI file can then be read in again, and the refine procedure started.

If a systematic error is seen to be present in the Indexing of Reflections table, an extrapolation factor must be determined. A small final precision value must be used when determining the error function.

If zero or a very limited number of lines are explained by this automatic Indexing, first, repeat a Refinement with zero iteration steps and a large final precision to allow more reflections to show in the Reflections table. If still zero or a very limited number of lines are explained, two cases should be considered:

1. The DI file contains the reflections of only one phase. The selected lattice parameter set is not accurate enough.
   - Enter better lattice parameters (refer to Chapter 11.5.4.1).
   - Increase the number of reflections to refine on.
2. The DI file contains more than one phase:
   - Select another 2θ range for refinement using "minimum and maximum two theta" that contains reflections relevant to the phase of interest. (Make sure that the reflections with the lowest hkl indices are present in the two theta range).
   - Increase the number of reflections to refine on.

11.5.4.3 Refinement

If it is sure that the DI file is reduced and contains K-alpha$_1$ reflections only, and that the starting set of lattice parameters is close enough, the actual refine procedure can be started.

This refine procedure should include a refinement on the extrapolation factor as the observed data and the lattice parameters input contain sytematic errors.

Finally if the refinement procedure for all phases present is finished, it is possible to correct the angle with the extrapolation factor and use the thus corrected DI file for further data analysis.

11.6 STRESS ANALYSIS

11.6.1 INTRODUCTION

The amount and the direction of stress in construction materials are important data relating to the reliability (maximum load) and lifetime (fatique) of constructions, machines, engine parts and so on. It can also be of equal importance to know the stress in metal parts between subsequent steps in the production process: if too much stress is present, the next step could be fatal for the product.

Stress is caused by forces in material. These forces can be applied momentary, more often they were generated during previous treatment of the (metal) part: residual stress.

Examples of possible causes of residual stress are:

- mechanical processes: surface working (shot peening, surface rolling), forming, assembling
- thermal processes: welding, casting, heat treatment
- chemical processes: corrosion, electro-plating

The forces acting in the metal part change the inter-planar distances in the crystallites. X-ray diffraction is the way to measure inter-planar distances, it can therefore be used for non-destructive stress determination.

Figure 11.14 illustrates how crystallites in different orientations will deform under stress. The dotted circle segment indicates the 'unstressed' situation with d_u. The distance between the lattice planes parallel to the surface is d_o, this is when the bisector of the primary and diffracted beams coincides with the normal to the surface which is analysed. If the sample is measured when tilted over an angle ψ (psi), the value d_ψ can be determined (see figure 11.15).

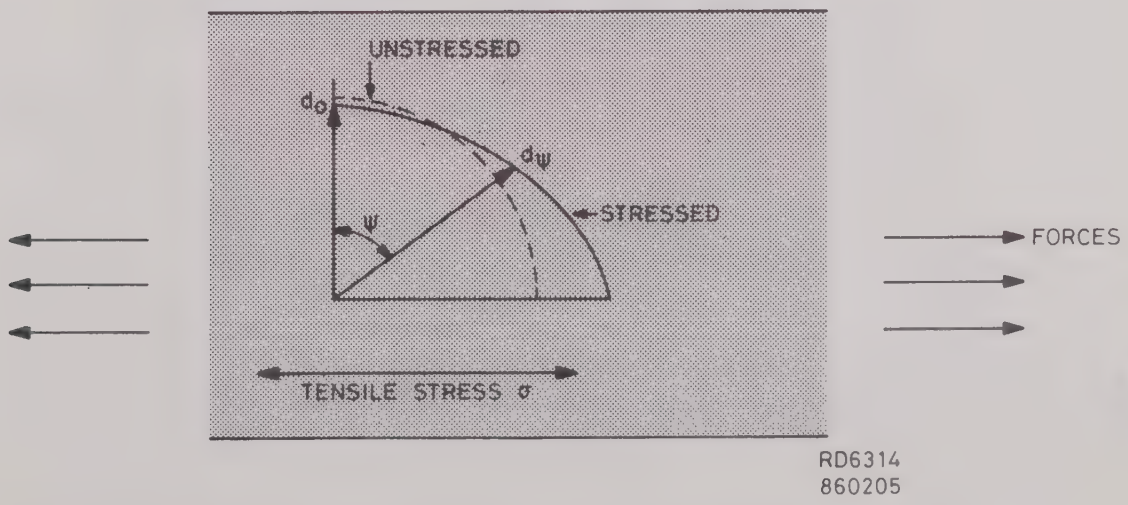

Figure 11.14 Influence of tensile stress on d-values of crystallites in various orientations

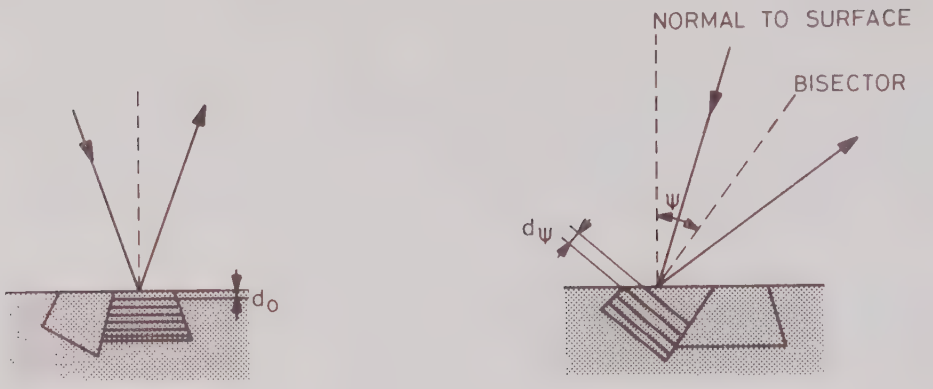

Figure 11.15 Measurement of d-values at different ψ angles

The relative change in d-value due to the stressed situation is:

$$\frac{d_\psi - d_o}{d_o} = \frac{1+\nu}{E} \times \sigma \times \sin^2\psi \text{ , where:}$$

ψ = tilting angle of sample ($\psi = 0$ is the symmetrical geometry)
ν = Poisson´s ratio (constant of traverse contraction)
E = Young´s modulus (elasticity modulus)
σ = stress = E .ϵ (Hook´s law)
ϵ = strain = $\frac{\Delta l}{l}$ (elongation or compression)

11.6.2 REFERENCES

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11.6.3 SYSTEM PREPARATION AND DATA COLLECTION

In order to determine stress in a sample with the APD STRESS ANALYSIS program (PW1868), a separate theta-drive PW1397 is required on the goniometer. Sample spinning is not normally allowed during stress measurements. It is advisable to choose as high a 2θ angle as possible to measure the d-values, taking into account that a peak without overlap is required (K-alpha$_{1,2}$ doublet is allowed as K-alpha$_2$ stripping can be performed) and that a stronger reflection gives shorter measurement time for the required precision.

For high intensities you could use a wide receiving slit (0.3 mm or 2 degree scatter slit which is about 0.8 mm), for very broad and low profiles you could remove the secondary Soller collimators (behind the receiving slit). For psi scans it is advisable to use a narrow divergence slit (1/2 degree; an automatic divergence slit can be decoupled at 14° 2θ and fixed) in order to avoid excessive line broadening due to defocussing. For the same reason (restricted defocussing) it is better to choose positive psi values only, together with the obligatory one or more zero-psi scans.

You have to assemble an analysis program, type "SCANS ONLY" containing a number of psi scans. You also have to assemble the goniometer scans of the type "PSI SCAN". We advise that the scans start and finish on a ´real background´. The different scan ranges should be compatible (the easiest way is to take the same starting and final angles for all scans used in one analysis). There should be scans with at least three different psi values, and at least one scan with psi = zero. The maximum value of psi should be smaller than half of the scan starting angle. The system will check the latter four requirements before you can start the stress calculations.

Data collection results in a raw data file containing the different psi scans. Without pattern treatment you may use the options of the "ANALYSIS, STRESS" program.

11.6.4 STRESS ANALYSIS

If you enter "S" in the ANALYSIS program the stress analysis program displays a menu of options which can be used to analyse the measurement results interactively. The commands are described in the following sections.

11.6.4.1 Files

Up to four raw data files can be defined for stress calculation. The maximum number of psi scans is 16. The sequence of the psi values is voluntary. File names are stored (in DEFAULTS.APD) for future use until you remove them. If you give the command "FILES" again, then the files that were entered previously are suggested as defaults. If you enter "0" (zero) instead of RETURN or a file name, the suggested file is removed from the list (in DEFAULTS.APD) and the following files move up one place in the list. If you enter "/" the suggested file and all following files are removed from the list.

11.6.4.2 Stress

When the "STRESS" option is selected the program automatically performs the calculations using parameters specified in "OPTIONS/DEFAULTS", and finishes by displaying the results as shown in figure 11.16.

```
APD STRESS ANALYSIS                                          12-FEB-86  13:53
-------------------------------------------------------------------------------

Sample identification: ALSHOT

Data file name      1 : [300,203]ALSHOT.RD

 Scan      Psi          2          Spacing       Actual       Act-Calc
number     (deg)    Sin (Psi)     D (Ang)        dD/D          dD/D
-------------------------------------------------------------------------------
    1       0.00      0.0000      0.82764      0.00000       0.00002
    2      30.00      0.2500      0.82714     -0.00060      -0.00004
    3      45.00      0.5000      0.82674     -0.00108       0.00002

Stress: -116 MPa  (Young's modulus: 70 GPa, Poisson's ratio: 0.290)
```

Figure 11.16 Output of stress analysis on Al sample

In this table the first three columns are self-explanatory, the fourth column displays the d-values calculated from the peak positions for the different psi angles. The fifth column tabulates the relative difference in d-values delta d/d (related to d_o: the average of the scans with psi = 0). A straight line through the points (in a plot delta d/d vs. sin square (psi)) is calculated using a least squares method. The difference between the measured (actual) points and the calculated line is displayed in the sixth column.

NOTE: There must be scans with at least three different psi values, including psi = 0. The system checks this requirement and will not perform the stress analysis if the requirement is not met.

The output of the stress analysis is followed by the menu: "Exclude, Include scans, Recalculate peak positions, Plot = Plot :=".

Exclude - With this option you can exclude one or more scans from the following stress calculation. Such scans wil be displayed in the output table marked with "*".

A new stress calculation will be done automatically and the output table will be displayed.

Include scans - This command is used to re-include scans that were previously excluded.

A new stress calculation will be done automatically and the output table will be displayed.

Recalculate peak positions - Individual peak positions can be calculated using parameters that are different to those used in the previous calculation. The system requests a scan number, then all parameters for the calculation of intensity correction and peak position can be subsequently altered. You can change the same parameters as in Options/defaults plus the number of background data points. Limits are 1 to half the points of the profile. If you enter "?" instead of a value or code, help text will be displayed for all of the parameters.

After the last parameter has been entered, the peak position is calculated and displayed. The system then requests whether or not you wish to recalculate more peak positions; if you enter "No" the stress is automatically calculated using the new peak positions.

NOTE: If you enter the number of a scan that previously has been excluded, it will then be automatically re-included for the subsequent stress analysis.

Plot - A plot of the peak positions of all the scans entered with "FILES" is made in a graph of delta d/d versus sin square (psi). Scans with positive psi angles are indicated by "+" and negative psi values by "*".

Excluded scans are indicated by "0" and "." respectively.

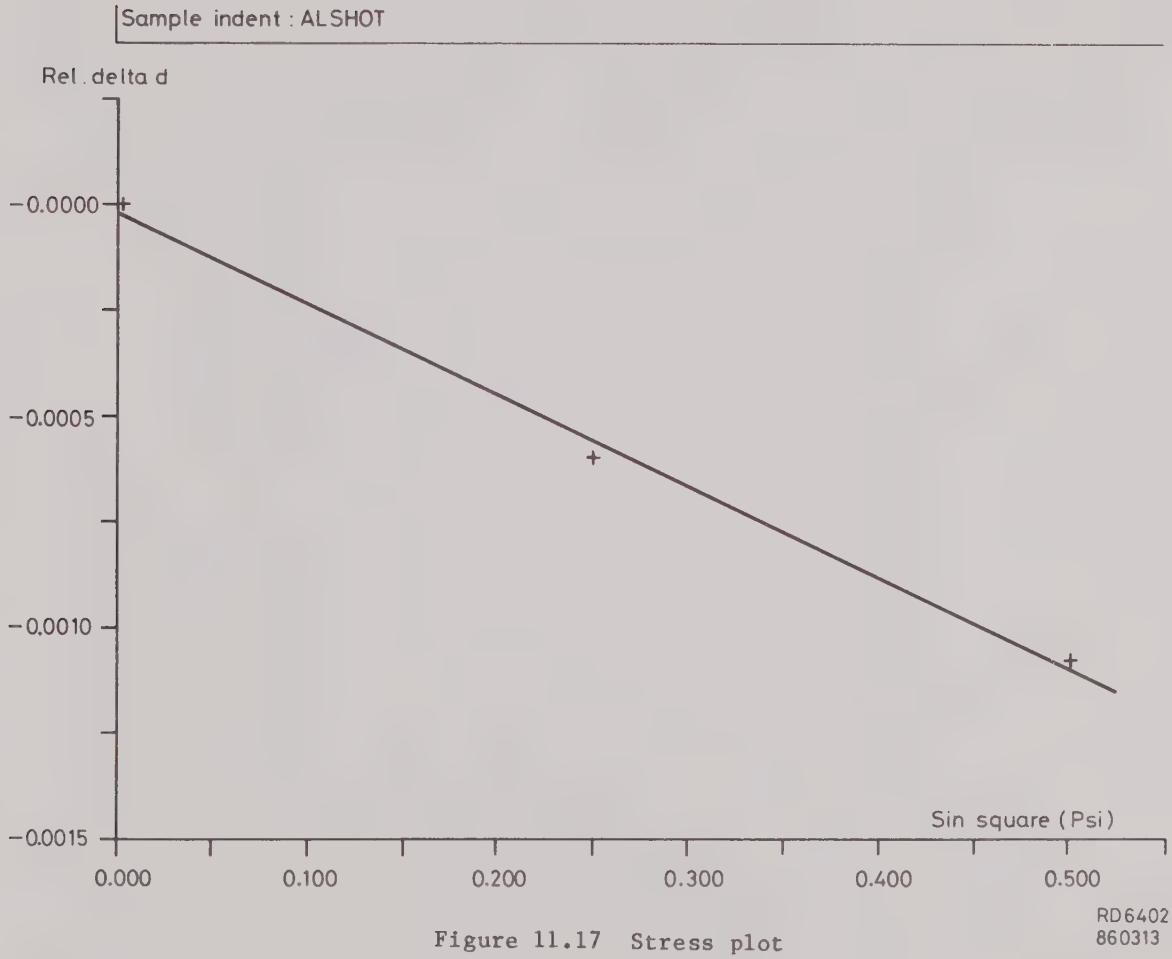

Figure 11.17 Stress plot

The calculated stress output table is displayed when you return from the graphics to the dialogue mode (by giving RETURN).

11.6.4.3 Edit Constants

This option can be used to define (depending on the sample material) Young's modulus and Poisson's ratio. Young's modulus and Poisson's ratio will be stored in the raw data file.

11.6.4.4 List

You may List scans or constants with this command. "LIST, Scans" tabulates the 2θ and psi angles for all the scans of the files specified with the "FILES" command. "LIST, Constants" displays Young's modulus and Poisson's ratio for each raw data file.

11.6.4.5 Options/defaults

You can change the defaults for printed output, intensity correction parameters and/or the peak match profile.

NOTE: If you enter "?" in the main stress menu current settings of the Options/defaults are displayed.

Printed Report

Three options are available: no printed report, a summary of the stress calculations as illustrated in figure 11.18, or the measurement data, correction steps and peak fit results of all the psi scans are printed together with the summary.

```
APD STRESS ANALYSIS                                          12-FEB-86  13:53
-------------------------------------------------------------------------------

Sample identification: ALSHOT

 Scan       Psi          2          Spacing      Actual       Act-Calc
number     (deg)     Sin (Psi)     D (Ang)       dD/D          dD/D
-------------------------------------------------------------------------------
    1       0.00       0.0000      0.82764      0.00000       0.00002
    2      30.00       0.2500      0.82714     -0.00060      -0.00004
    3      45.00       0.5000      0.82674     -0.00108       0.00002

Stress: -116 MPa  (Young's modulus: 70 GPa, Poisson's ratio: 0.290)

Exclude, Include scans, Recalculate peak positions, Plot = Plot := /
```

Figure 11.18 Output table with summary of stress calculations

```
APD STRESS ANALYSIS                                          12-FEB-86  13:52
-------------------------------------------------------------------------------

Sample identification          : ALSHOT
Data file name                 : [300,203]ALSHOT.RD

Scan number                    :            3
Angle range measured (deg)     : 134.5000 - 140.5000
Angle range considered (deg)   : 134.5000 - 140.5000
Stepsize, Number of data points:   0.0200          301
                2
Psi angle (deg),Sin (psi)      :  45.00        0.5000
Background: data points used   : First  15 & last  15
          level, slope         : 0.2288E+03 0.1042E+00
No monochromator used
Lorentz polarization factor    :      Code = 2
Absorption correction applied
LP factor / Absorption factor  :           1.3
Alpha2/1 intensity ratio       :           0.5000
Peak angle (deg), Spacing(Ang)
     fitting a parabola        : 137.4118      0.82674
     fitting a gaussian        : 137.4292      0.82669
     fitting a Cauchy/Lorentz  : 137.4284      0.82670
Used peak fit                  :        Parabola
Halfwidth, asymmetry           :   1.100           1.099
Integral breadth, asymmetry    :   1.379           1.047
```

Figure 11.19 Output of peak match for stress analysis

NOTE: ND (Not Determined) for the halfwidth, integral breadth and the asymmetries of the peaks if no alpha$_2$ stripping is done.

Background Correction

You can choose to apply no background correction at all, or you may choose for ´automatic´ linear or parabolic background fitting, have the system choose the best of the two profiles (optimal), or manually define background parameters.

If you choose a parabolic background shape the program tries to fit a ´valley type´ parabola, if it does not succeed the system calculates a linear background.

If the background is known, for example from previous experiments, then you could choose manual background definition. You can specify the background "level" (A), its "slope" (B), and the "curvature" (C) in the background formula: Background = $A + BX + CX^2$, where X = the number of measurement data points (the lowest angle in the "angle range considered" is the data point with X = 1). If you want to define a linear background you choose C = 0.

NOTE: The number of data points at the low end and at the high angle end of the angle range considered during calculation is by default: The number of data points in the angle range considered divided by 20, with a minimum of 5 points. This can be changed with the "Recalculate peak positions" option (refer to Section 11.6.4.2).

Lorentz-polarization Correction

The measured intensity can be corrected by dividing it by the Lorentz-polarization factor. Correction for the angle dependent Lp factor can be done using any one of five code numbers. Code numbers 1 and 2 are used for correction of diffraction peaks of polycrystalline materials. If you define code=1 then a formula which is appropriate for correction of a diffraction peak total is used (integrated counts). For correction of step scan results you define code=2, this will normally be the situation with this program. For correction of diffraction profiles of materials which are (very similar to) single crystals you should select code=3 instead of 1, and code=4 instead of 2 for the two different measurement methods. It is not very likely that thistype of material will be analysed in this way. If you choose code=5 no Lorentz-polarization correction will be performed.

The formulas are as follows:

Code number	Formula
1	$\frac{1 + POL \cdot \cos^2 2\theta}{\sin^2 \theta \cdot \cos \theta}$
2	$\frac{1 + POL \cdot \cos^2 2\theta}{\sin^2 \theta}$
3	$\frac{1 + POL \cdot \cos^2 2\theta}{\sin \theta \cdot \cos \theta}$
4	$\frac{1 + POL \cdot \cos^2 2\theta}{\sin \theta}$
5	No correction

POL describes the extra polarization owing to the use of a monochromator:

$POL = \cos^2 2\theta_{mon}$

where $2\theta_{mon}$ is the diffraction angle of the monochromator. If no monochromator is used POL = 1. Since the system knows if a (graphite) monochromator was used it selects the correct value automatically. POL is equal to 0.8 for Cu K-alpha with a graphite crystal.

Absorption Correction

The x-ray path length through the specimen is longer in asymmetric situations (psi ≠ 0) than in the symmetrical case when psi = 0. Measured intensities should be corrected by dividing it by the absorption factor calculated from:

$$1 - \tan psi \cdot \cot \theta$$

Alpha$_2$ Stripping

In most cases it is advised to eliminate the K-alpha$_2$ component of the measured profiles. The Alpha$_2$ stripping procedure uses the intensity ratio of the K-alpha doublet. Normally this ratio is very close to 0.5. If a monochromator is used, for very accurate work the ratio should be determined experimentally from the measurement of a profile at high angle (120^o to 150^o 2θ).

NOTE: If no background correction is specified, Alpha$_2$ stripping will not be done.

Peak Match

This includes the determination of Peak position, Halfwidth and Integral breadth. You may choose to have a Parobola, a Gaussian, or a Cauchy (Lorentzian) function to be fitted to the top part of the corrected profile to find the peak position, or to let the system determine which of the three functions yields the best fit (Optimal). The top part consists of the data points with intensities larger than 0.5, 0.7 or 0.85 times the highest corrected intensity (with a minimum of 5 data points) whichever gives the best fit.

The system applies all three functions and uses the one that fits best for the determination of the 2θ angles with half of the maximum intensity of the top just calculated. The difference of the 2θ angles gives the halfwidth of the profile (FWHM).

The sum of the counts of the data points in the angle range considered divided by the maximum intensity at the top as calculated, gives the integral breadth of the profile.

The calculated peak position is used to determine asymmetry of the profile in terms of halfwidth and of integral breadth. Asymmetry is defined as the low-angle part of the profile's breadth divided by the high-angle part with respect to the peak position.

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12.1 INTRODUCTION

Utilities is a set of auxiliary programs for various "non-routine" purposes:

- The CALCULATOR program allows you to do the type of calculations normally used in x-ray diffractometry.
- The FILE HANDLING utility is an easy-to-use set of disc file management commands in the APD1700 menu dialogue.
- PW1710 commands can be given "directly" from your terminal to the diffractometer control: the computer is in effect "transparant".

12.2 CALCULATOR

At your disposal are calculations which use Bragg´s law, Mass absorption coefficient, and the position of diffraction peaks for K-alpha and K-beta radiation.

12.2.1 BRAGG´S LAW

This utility enables you to convert d-spacings into theta values and vice versa with the use of Bragg´s formula. The system requests you to define the tube anode material (for the K-alpha$_1$ wavelength). Then you may enter:

D-spacing, Theta, or 2theta.

Output is: D-spacing, Theta, 2theta, Sin(theta), Sin^2(theta).

12.2.2 MASS ABSORPTION

This program can be used (for example as an auxiliary to Quantitative analysis) to calculate the mass absorption coefficient of chemical compounds and mixtures for the weighted K-alpha$_1$ and K-alpha$_2$ radiation of the tube type that you specify. The penetration depth and path length of the x-rays in such a sample are calculated if you enter the density of the sample and the angle.

You can choose between:
"Formulas, Mixture, Penetration, List, Options/defaults".

12.2.2.1 Formulas

The chemical composition of a pure compound is entered by its chemical formula.

NOTE: If the chemical composition of a sample is known in terms of elemental concentrations or oxides, then the elements or oxides can be introduced using the Formula command.

Formulas can be entered in two different ways, depending on your choice in Defaults. For both syntaxes the following rules apply:

- Elements can be separated by a space, an index number or parentheses.
- An element or a group of elements can be placed in parentheses. Nesting is not allowed.
- The index number - multiplication factor, or number of atoms per compound molecule - can be any positive number (between 0.0001 and 9999.9999).
- A dot (point) in a formula which is not being used as a decimal point must be preceeded by a space (for example: Cu2SO3 . H2O). All other spaces are skipped.

Exact input requires the following additional rules:

- Elements of one character: enter in upper case (capital).
- Elements of two characters: first character in upper case, second in lower case character.

Free case input has the following requirements:

- Elements can be entered in upper case and/or lower case characters.
- Elements can be separated by a space, an index number or parentheses.
- Two character elements are prior to one character elements,
- Left side elements prior to right side elements.

Examples of "free case" input (output is always in "exact case"):

Input	Interpretation	output
CO	Cobalt	Co
C O	Carbon-Oxygen	CO
CRU	Chromium-Uranium	CrU
C RU	Carbon-Ruthenium	CRu

The system uses the mass absorption coefficients of the elements (from: International Tables for X-ray Crystallography (Kynoch Press, 1974). Volume IV, p. 61-66) and the atomic weights (both tabulated in the system´s memory) and calculates the molecular weight and the mass absorption coefficient of the compound.

12.2.2.2 Mixture

After you have entered the formulas of the components of a sample, you can request to calculate the mass absorption coefficient of the mixture. You have to enter the weight fractions. If the sum of the weight fractions differs from 1 (more than 0.001), then the system requests whether you want to normalize to 1.000 or not. If you enter No, then you have to enter the weight fractions again. If you enter Yes, then the system will normalize the weight fractions so that the sum equals 1.000.

The system will also display for each component the value for I/Io. This is the intensity of a (representative) peak of the component in the mixture, divided by the intensity of the same peak for the pure compound material. For component i this is:

$$\frac{I_i}{I_{i0}} = \frac{W_i}{1.0} \cdot \frac{MAC_i}{MAC_m}$$

In this formula W_i is the weight fraction of compound i in mixture m.
If you want to enter a new set of formulas, enter "F". The "old" formulas will be displayed as defaults. You may change the formulas, or delete them by entering 0 (zero) for the formula.

12.2.2.3 Penetration

The system displays the mass absorption coefficient (MAC) which has most recently been calculated as default, you may change the value if you want.

Then the system requests you to enter the "density" of the sample, this value should combine the specific gravity (= density) and the (estimated) packing density (1 minus the hollow fraction of the sample volume). The packing density for (manually) compressed fine powder ranges roughly from 0.5 to 1.0, this means that, for example, the "density" value of quartz (SiO_2, specific gravity = 2.65) lies between 1.33 and 2.65g/cm^3.

Next the diffraction angle (degrees 2 theta) for which the penetration must be calculated is requested.

Firstly the "Path length" is calculated, that is the length of path of an x-ray through the sample material which just transmits 1% the diffracted intensity.

Then the "Penetration depth" is established: that is the thickness of the sample which gives 99% of the diffracted intensity. Integration of the contribution of subsequent layers of sample material gives the diffracted intensity. In theory this integration has to be extended to infinity. For practical purposes the above-mentioned fraction of 99% give a better impression of the effective volume of the sample.

NOTE: Half of the calculated depth will diffract 90% of the infinite sample intensity, a quarter of the calculated depth will diffract 68% of the infinite intensity. Double depth will diffract 99.9%.

The method:

The calculation uses the formula as described by: Baldock, P.J. & Parker, A. J. Appl. Cryst (1973) 6 ,153):

$$I = Io \times \exp\left(\frac{-Mu \times t\ (1-v)}{\sin\theta}\right)$$

Here: I = the diffracted intensity at depth t
Io = the diffracted intensity at depth 0 (zero)
Mu = linear absorption coefficient of the sample (cm^{-1})
t = depth under sample surface (cm)
v = volume fraction not filled with sample material (the hollow part)

The program calculates Mu (1-v) = MAC x density, this gives the path length 1 = 2t/sin θ which transmits 1%, that means I/Io = 0.01.

exp (-MAC x 1 x density) = 0.01
MAC x 1 x density = ln 100 = 4.6052
1 = 4.6052/MAC x density (cm)

The output gives the path length in /um (10^{-6}m):

Path = 46052/MAC x density

The penetration depth t is calculated from the integral:

$$I = \int_0^t Io \times \exp\left(-\frac{2MAC \times t \times density}{\sin\theta}\right) dt$$

$$I = \frac{\sin\theta}{2MAC \times t \times density} \times Io \left[1 - \exp\left(-\frac{2MAC \times t \times density}{\sin\theta}\right)\right]$$

For an infinitely thick sample:

$$Iinf = \frac{\sin\theta}{2MAC \times t \times density} \times Io$$

The thickness where the intensity equals 99% of Iinf:

$$\left[1 - \exp\left(-\frac{2MAC \times t \times density}{\sin\theta}\right)\right] = 0.99$$

or:

$$\exp\left(-\frac{2MAC \times t \times density}{\sin\theta}\right) = 0.01$$

$$\frac{2MAC \times t \times density}{\sin\theta} = \ln 100 = 4.6052$$

$$t = \frac{4.6052 \times \sin\theta}{2MAC \times density} (cm)$$

also $t = l \times \frac{\sin\theta}{2}$, therefore the penetration depth in /um equals:

$$Depth = Path \times \frac{\sin\theta}{2}$$

12.2.3 ALPHA/BETA

The program establishes the diffraction angles (2 theta) of the K-alpha$_1$, K-alpha$_2$, K-alpha$_{1+2}$ (Alpha *) and K-beta lines when you input the angle of one of those lines.

NOTE: These calculations are made by the system to correct the lines in a DI file. Refer to Analysis, Identify, New DI file command (Chapter 11.2.3) and Edit Alpha$_1$ peaks (Chapter 11.2.12).

You may choose the tube anode material : "Cu, Mo, Co, Fe, Cr, Other". For the five elements the wavelengths and their ratios are stored in the memory. If you choose "Other" tube type, you can enter the values of the wavelengths (Angstrom) for the K-alpha$_1$, K-alpha$_2$, and K-beta lines.

12.3 FILE HANDLING

A set of commands for disc file management. It is a subset of the file handling possibilities of the RSX system plus a special combined command.

* Sort re-arranges the files in alphabetical order for a surveyable directory.
* Copy (groups of) files from your or other UFD´s to yours.
* Delete one file at a time.
* Rename a file if required.
* Tidy up means: delete all "secondary" data files in your UFD, but not RD, DI and QI files.
* List directory gives a list of files in a UFD, your UFD is default.

"Wild cards" (asterisk *) can be used to indicate files with any name, any extension, and/or any version. Wild cards cannot be used for Delete (except for version number).

Refer to Chapter 2.3 for more detail on file management.

12.4 PW1710 COMMANDS

These commands make the computer "transparent" so that you can send all microprocessor commands directly to the PW1710 diffractometer control. On a TEKTRONIX 40xx graphics terminal, the RESET PAGE will not be automatic. Refer to the PW1710 Operating Manual for use of the commands.

Using ESC(APE) or CTRL/Z makes you return to the UTILITIES menu.

13.1 LIST

All parameter files that have been assembled, all reference patterns, and all data files (except for EC and SF files) can be listed on your terminal or on the system printer. The contents of the tables of wavelengths and MAC's (refer to Chapter 7.6) can also be listed. The output can also be written in a list file (an ASCII file).

For List Ref(erence) patterns you must enter the reference number (PDF or user pattern). In IDENTIFY (SANDMAN) and SYSTEM PREPARATION, REFERENCE DATA BASE you can choose to display: Mineral name or Formula, Angles or D-values, and Normalized intensities or Counts (in OPTIONS/DEFAULTS, Representation).

If List Data file has been chosen, then the system requests a file name. As in all situations where a file name is requested, the system proposes the last file name that was entered. The file type extension default for list is: DI (for example: Data file name = LAST.DI :=). If you want a different type (with the same name) then you should enter the file type extension preceeded by a point (for example: .SM or .RD).

In Options/defaults the length of the header, the length of the data and the output device can be chosen. If you choose "Optional" then when you want to list a file, the system will request what type of output you want, and on which device. The possible choices are:

"Header length: None, Short, Full, Optional:="

"Data: None, Short, Full, Optional:="

"Listing to: Terminal, Printer, File, Optional:="

NOTE: The command "LIST, LIST FILE" can only be given in order to print an ASCII-file (.LIS file).

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14.1 INTRODUCTION

In this chapter it is assumed that the system has been working properly. If it has not, then the Chapters on Installation (Chapters 7 to 10) in the System Software Manual should be used as a guide for the installation of (part of) your system.

If an error message is displayed when a problem occurs, read the explanation in Chapter 15 and if possible take the proposed action.

In the following sections some main groups of problems are described. Diagnosis is made simple, and remedial suggestions are made. The following problem types are dealt with:

1. Communication between terminal and computer.
2. Data collection; communication between PW1710 control and computer.
3. Reading of disc files.
4. Checkpoint space allocation.

If you have a problem, also refer to the ´List of known errors´.

14.2 COMMUNICATION TERMINAL/COMPUTER

Communication errors within the system can be a cause of problems. These problems can occur at place, or at several places in the system. The terminal status can be changed (for example the baud rate or the ON LINE/LOCAL switch).

The computer hardware can have a problem, or the software (operating system) may be in disorder. The connection cable between terminal and computer is another potential source of problems in communications.

In general these problems show themselves as one of the following:

- It is not possible to log in.
- The system does not respond to input, the terminal seems to ´hang´.
- Output from the system suddenly stops.

The following pages are meant as a diagnostic tool, actions to improve a fault situation are proposed.

PDP-11 or MICRO/PDP systems

1. At another terminal, give the command:

   "LOG SYSTEM/SYSTEM" and
   "SHOW TERMINAL TTn" (n = connection number of ´problem´ terminal).

   If the output contains the word "SLAVE", then give:

   "SET TERMINAL TTn/NOSLAVE".

2. If the prompt is "DCL>", then give "SHOW ACT".
   If the prompt is "MCR>", then give "ACT".
   A list of active tasks will be given.

   A task can be aborted by entering:

   "ABO taskname"

   Where taskname must be one of the names shown by the SHO ACT command.

3. At another terminal, give: "LOG SYSTEM/SYSTEM" and request a display of a list of the terminals which are connected to the Queue Manager:

   "SHOW QUE"

   If the "problem" terminal (TTn) is Queued, give:

   "@LBO:[1,2]STOPPR"
   As shown in the following example:

4. Check the communications protocol of the terminal.

5. Find the defective cable, defective terminal, or bad terminal connection at the computer interface by exchanging (parts) with other terminals.

6. Follow the flow chart in figure 14.1.

Professional 350/380 system

See The Chapter about problem solving in you Professional Owner´s Manual.

14.3 DATA COLLECTION; CONNECTION PW1710/COMPUTER

Problems during Data collection can be for example:

- Data collection does not start.
- Data collection suddenly stops.

The error can be in the PW1710 control, or in the computer software, the connection cable between PW1710 and computer can be another cause of problems. It is also possible that the required diffractometer is already under the control of another terminal in the transparent mode, via the "UTILITIES, PW1710" command.

Figure 14.2 provides a diagnostic tool and proposes actions to overcome the problem.

14.4 READING OF DISC FILES

Any problems that occur during reading of disc files can have very diverse causes. If an error message is given, this usually also refers to a Fortran error code or a FCS-code. Refer to Chapter 15 for an explanation of the error messages.

Other problems can be:

1. The file(s) is locked.

   Request a directory: files that are locked are indicated by "L". The locked file may not be displayed in your directory because it is in another UFD, for instance, one or more of the files of the PDF data base may be locked. Request a directory of DL1:[300,57] for the Inorganic data base, DL1:[300,56] for Organic, or DLx:[300,60] for the User Reference data base or the UFDs in use with a Professional 350/380 system.

   Action : Use the command "UNLOCK" for each locked file. Refer to the Software Instruction Manual Chapter 4.3.

2. If you start APD when you are in a UFD which has not been CREATED, then the message: "Error in system parameter file" is displayed.

   Action : Log in using an existing UFD.

3. A disc must have been MOUNTED before you can read a file from it. If there is doubt, request (does not apply to Professional 350/380 systems):
   "SHOW DEVICE DL1:". If the system displays:
   "DL1: Public Loaded Type=RL02" instead of:
   "DL1: Public Mounted Loaded Type=RL02",
   then the disc must be mounted. Use the command "MCR MNT DL1", refer to the Software Instruction Manual Chapter 4.4.

4. A file can be PROTECTED in such a way that you cannot use it. This can have several causes:

   a. The file has been protected on purpose.
      Action : You should not be trying to use the file in the way that you tried.

   b. The file owner is in another user group.
      Action : Log in your own UFD, copy the file to your UFD (or group).

   c. If a problem had occurred which gave an error message advising copying of the System Parameter file from the ´master´ disc, then the PROTECTION of the file should have been changed after the copy procedure.
      Action : Refer to paragraph 14.4.1 for the complete procedure.

   NOTE: You can display the protection code for files with the command: "DIR/FULL (filenames)". Refer to the Software Instruction Manual Chapter 4.3.

14.4.1 TO COPY THE SYSTEM PARAMETER FILE FROM THE ´MASTER´ DISC

In the message "Error in system parameter file" you are instructed to copy the ´master´ disc.

If the complete disc is copied, all the data files must also be copied from the ´problem´ disc. In many instances it is easier to copy only the system parameter file APDSYS.DAT from the master disc. After that the PROTECTION of the file must be changed.

The following steps ´a´ to ´i´ list the procedure required to copy the file and set the correct protection (PDP-11 or MICRO-PDP systems):

a. "LOG SYSTEM/SYSTEM".
b. Dismount DL1 "MCR DMT DL1".
c. Insert the "master" disc in DL1 and mount it: "MCR MNT DL1".
d. "SET DEF [1,2]".
e. "COPY DL1:APDSYS.DAT APDSYS.DAT".
f. "SET PROT APDSYS.DAT WO:RWE".
g. Dismount DL1 "MCR DMT DL1".
h. Insert and mount the original DL1 "MCR MNT DL1".
i. "LOG".

The procedure for Professional 350/380 systems is to insert the ´master´ floppy disc and proceed with steps d, e and f.

14.5 CHECKPOINT SPACE

This section only applies to PDP-11 and MICRO/PDP systems.

If the console terminal (TT0) displays the message:

"<time> <name> Checkpoint space allocation failure"

then the following situation exists.

Checkpointing is the process by which the RSX system makes memory space available to higher-priority tasks. The lower-priority tasks are saved on the disc exactly as they are interrupted. For that purpose space must be allocated on the disc. The system start-up command file as delivered on the APD1700 system disc allocates 500 blocks of checkpoint space on both discs.

How much space is required depends on the number of users and the computer memory size. The combination of: many users, and a relatively small memory leads to the need for a larger checkpoint space.

If the system sends the message that there is not enough space under the existing circumstances, then double the number of blocks. First log in using a privileged UFD, and then first reset the checkpoint space to zero, then set the new space. Do that as follows:

"LOG SYSTEM/SYSTEM"
"SET DEVICE DLx /CHECKPOINT FILE: 0"
"SET DEVICE DLx /CHECKPOINT FILE: n" (n = required number of blocks)
"LOG"

If necessary, you can double the number of blocks again later.

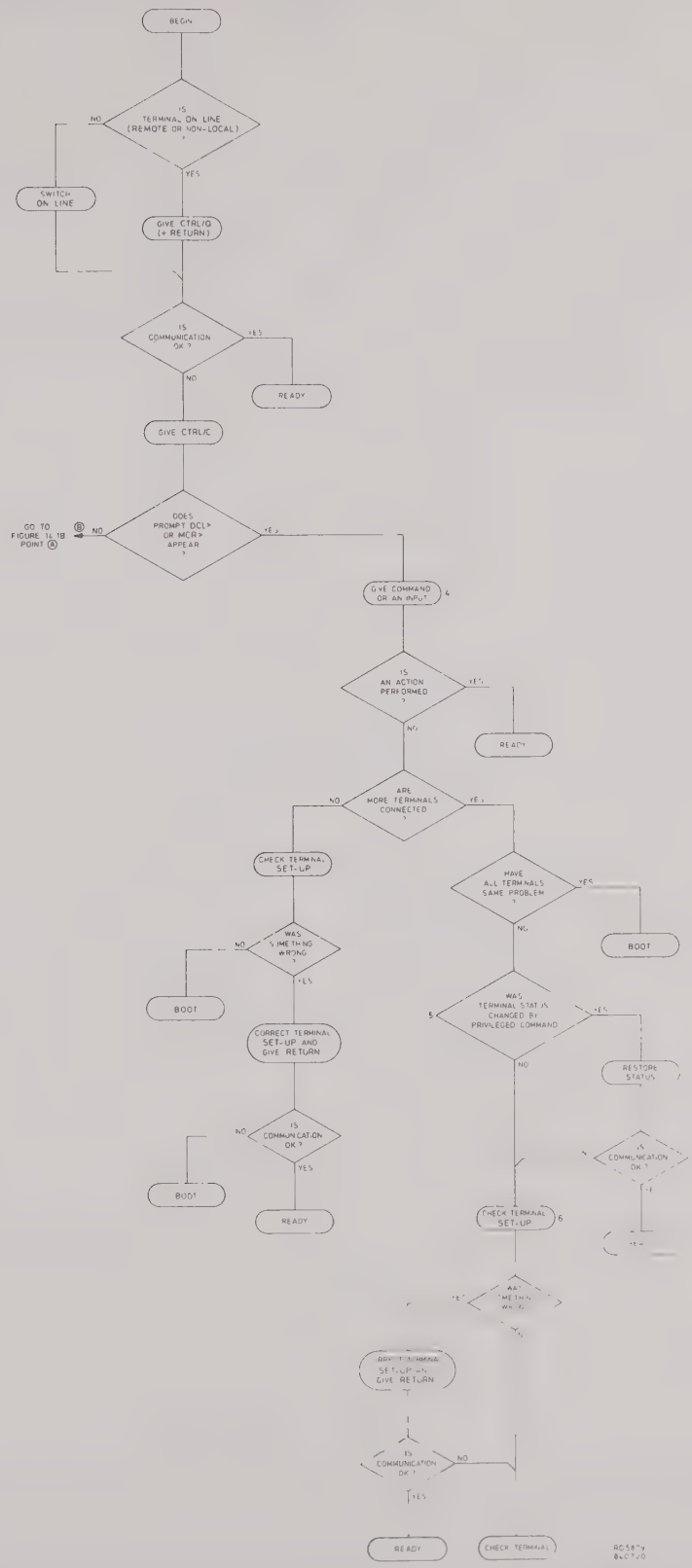

Figure 14.1A Communications Fault Finding Flow Chart (PDP-11 and MICRO/PDP)

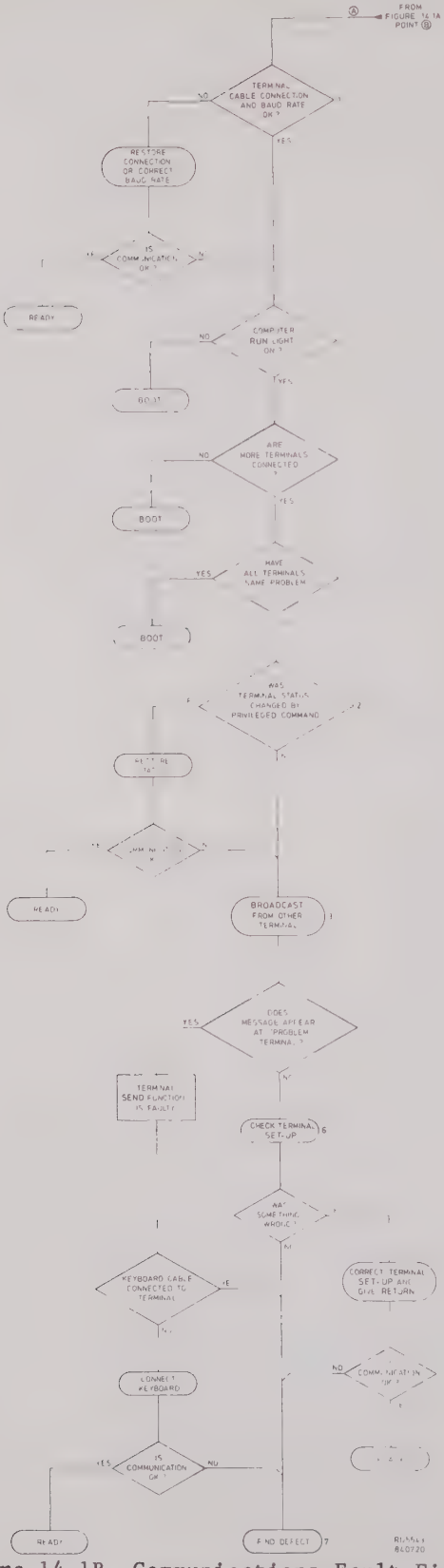

Figure 14.1B Communications Fault Finding Flow Chart (PDP-11 and MICRO/PDP)

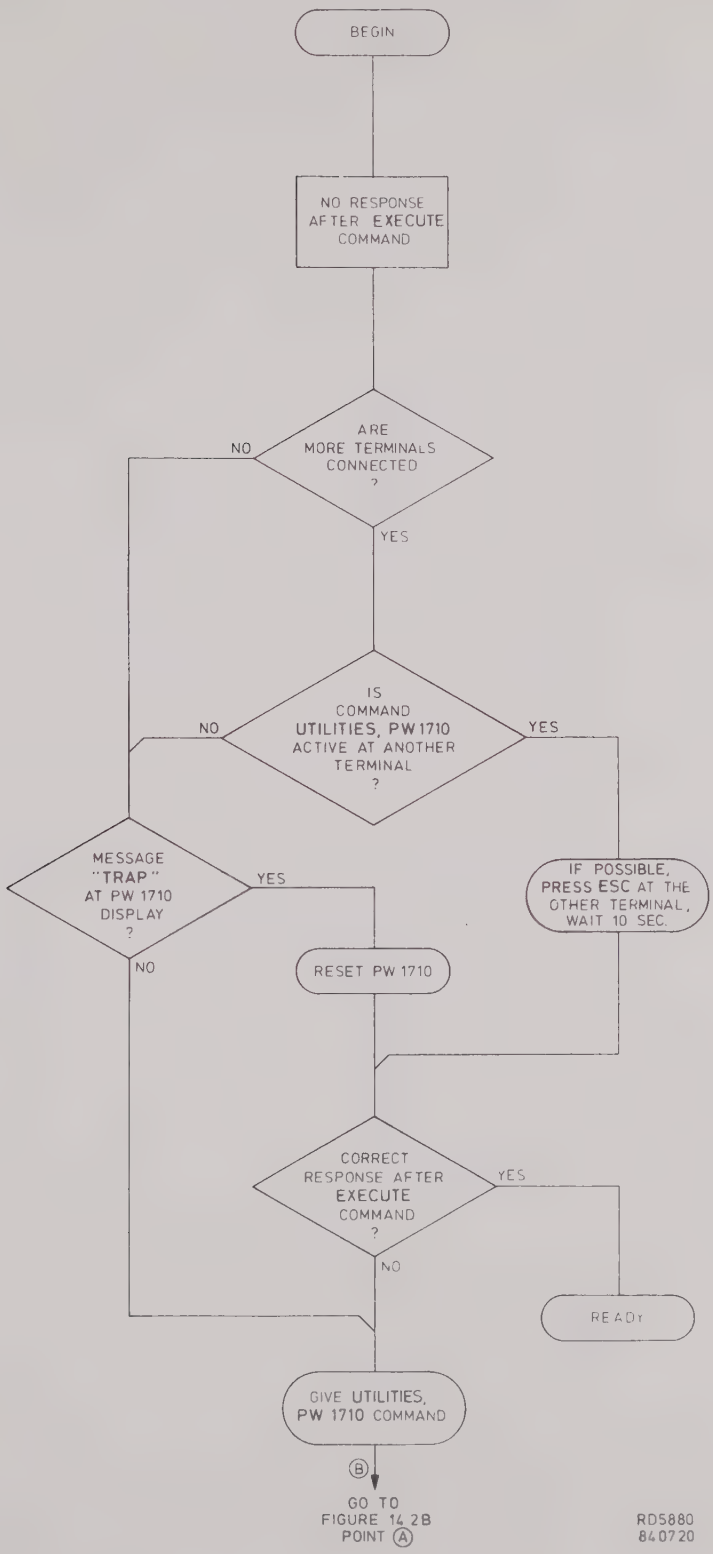

Figure 14.2A Data Collection Fault Finding Flow Chart (PDP-11 and MICRO/PDP)

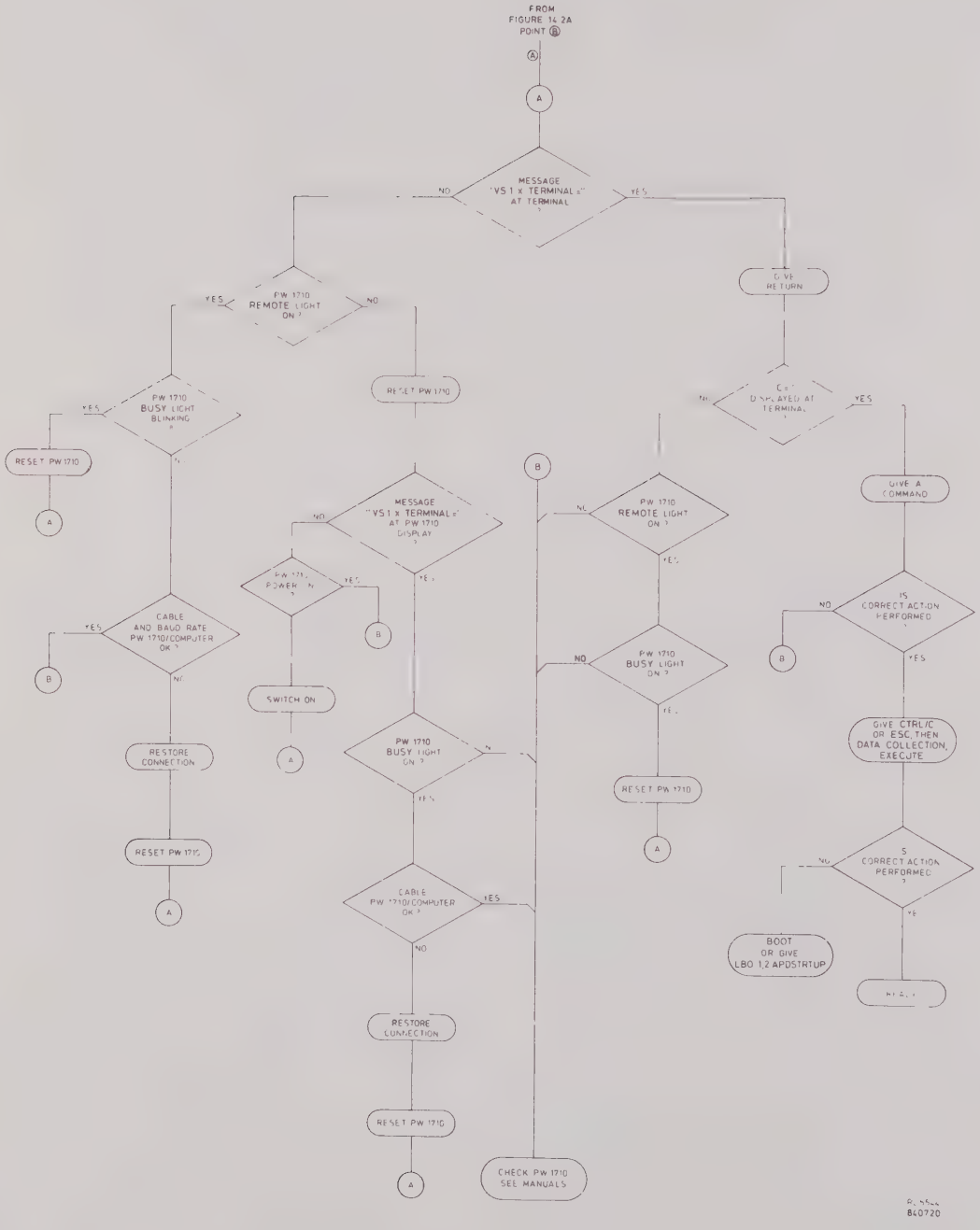

Figure 14.2B Data Collection Fault Finding Flow Chart (PDP-11 and MICRO/PDP)

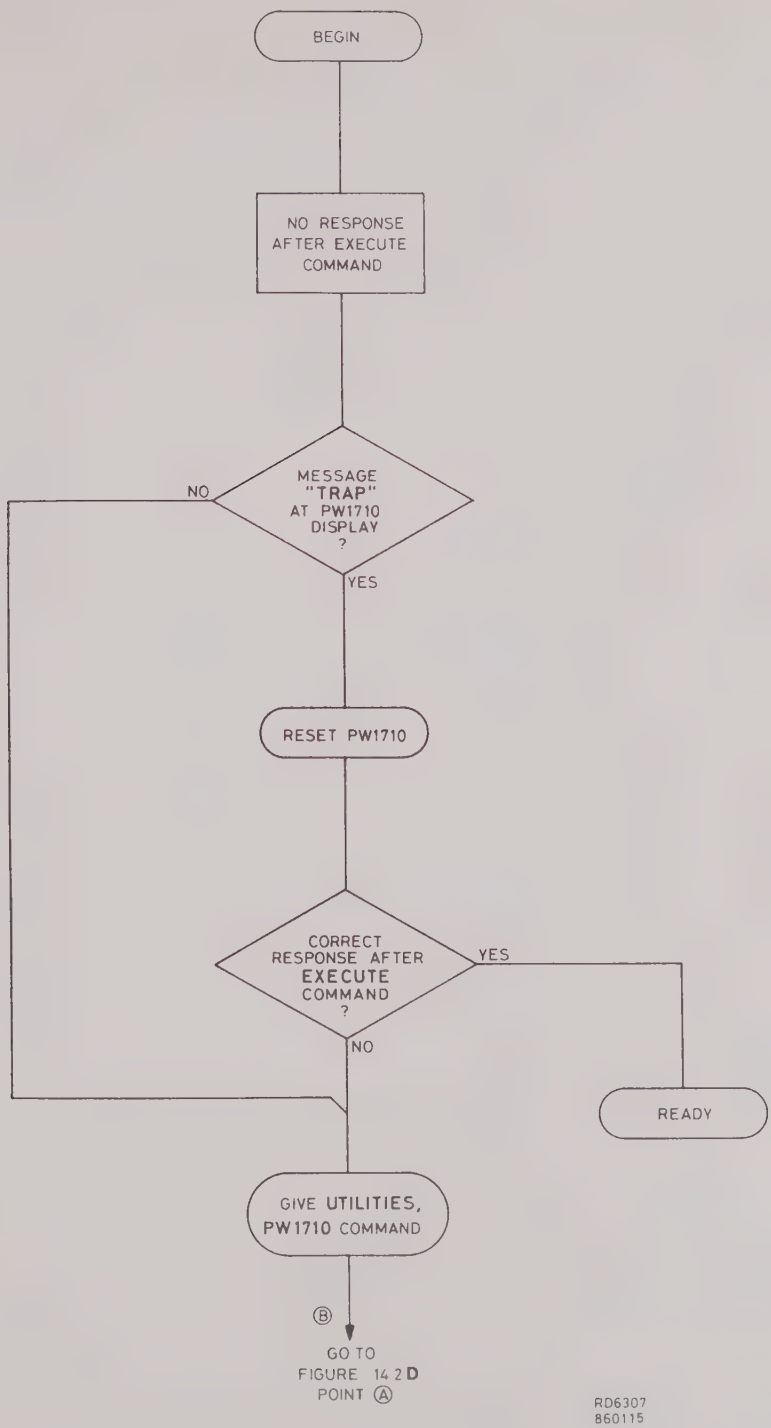

Figure 14.2C Data Collection Fault Finding Flow Chart (Professional 350/380)

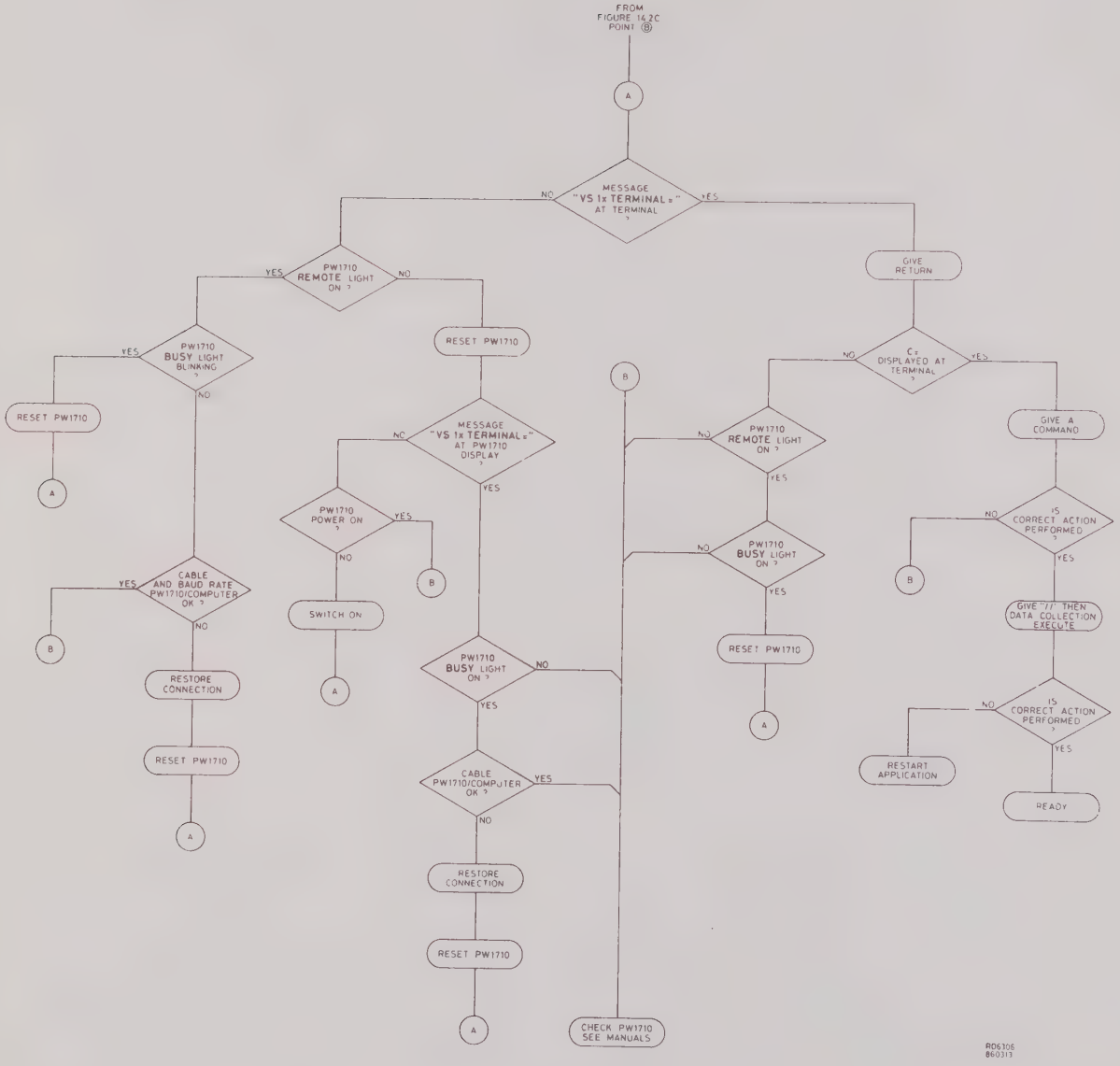

Figure 14.2D Data Collection Fault Finding Flow Chart (Professional 350/380)

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15.1 INTRODUCTION

This chapter provides three lists of error messages:

APD1700 Messages
FORTRAN Errors
FCS

Some error messages may appear during dialogue, they are all self-explanatory and are not given or explained in this chapter.

Sometimes the message action will require you to send us a Software Performance Report (SPR). This report can be found with the preface pages at the front of this manual. The necessary information that you need to complete the report will be displayed if you give the command "SPRAPD" as described in the Software Instruction Manual Chapter 4.4. If there is a unit number given in the error message, make a note of this number as you will need it later.

15.2 APD1700 MESSAGES

There are two groups of APD messages, the first group of 24 are produced by the PW1710 (15.2.1), and the remainder are produced by the APD software (15.2.2).

15.2.1 DIFFRACTOMETER ERRORS (PW1710 MESSAGES)

Error messages and/or warnings from the PW1710 can come from any of the connected Diffractometer systems (up to four are allowed). The number of the faulty system is included in the message. The messages are always in the following format (error 17 is only given as an example):

```
*** ERROR ON DIFFRACTOMETER SYSTEM n
*** ERROR 17
```

There are 24 error messages that can be produced by the PW1710, they are as follows:

nn		MEANING
1	ILLEGAL ARGUM.	The argument specified in the last command is either: missing, or has the wrong format, or is outside the specified range.
2	UNKNOWN COMMAND	The command (mnemonic) that you have just given cannot be found in the command list.
3	MEMORY OVERFLOW	The available memory area is filled, too many programs, and/or too many registers have been specified.
4	ILLEGAL COMMAND	The last command given is known, but not allowed in this situation.
5	LIST OVERFLOW	The program you are writing is too long (maximum length = 255 bytes), split it into parts and link them.
6	STACK OVERFLOW	Too many program calls have been nested (maximum = 6).
7	NOT IN MEMORY	One of the programs involved is not in memory.
8	UNKNOWN CODE	During PRP or CLP, a command code is found that cannot be translated into a command. Error in memory chip.
9	TRANSM.ERROR	A parity, framing or overrun error has occurred in a transmission with a terminal or a computer.
10	BATTERY ERROR	Back-up battery empty, all the programs are lost and all the parameters are cleared. Refer to chapter 5.7.6.
11	OUT OF RANGE	In a the command just given to set an angle, the angle requested is either negative or out of range.
12	ILLEGAL REGIST.	The register addressed has not been declared.
13	GONIOMETER LIMIT	One of the goniometer limit switches has been activated.
14	NO 2ND OUTPUT	Output to a second output device is not possible; switch the device on or give a DOF command.
15	RECORDER ERROR	The strip chart recorder is in local mode or has no paper or is not connected.
16	TIME OVERFLOW	The total measuring time is more than 3 276.75 seconds.
17	CHANGER ERROR	A Sample Changer error: it can be, a mechanical defect, or the command has not been allowed because of the sample changer status.
18	NO CHANGER	The sample changer is not connected.
19	SAMPLE IN GON.	Sample already in goniometer (load command not allowed).
20	SAMPLE IN MAG.	Sample in magazine (unload command not allowed).

21 NO SAMPLE	Load command given, but there is no sample available.
22 NO I/O DEVICE	There is no cassette recorder (RME and WME).
23 CASSETTE ERROR	The recorder was not in STANDBY, or the cassette was not in a "end of data" gap, or no cassette was mounted, or a cassette with a write disable plug was mounted.
24 NO DATA ON TAPE	The RME command was given, but there were no PW1710 programs on the cassette.

15.2.2 APD MESSAGES

The APD messages appear with the following format:

*** ERROR nnn Text of message.

There are 56 messages. They are all given below in numerical sequence together with their content and if necessary any rectification steps and/or suggestions:

51 No information of this diffractometer number available. Assemble System Parameters, Diffractometer part.

52 *** Subroutine not YET available ***

54 I/O error on PW1710 line, try: Utilities, PW1710 commands.

55 PW1710 sent "TERMINAL=", it has been reset at an unexpected moment.

56 A Software error occured. Boot the system (or give @LBO:[1,2]APDSTRTUP). If the problem persists please send a Software Performance Report.

57 File is not of appropriate type. Possibly another type of file has been "renamed", and the new name included the WK file type specifier.

58 The Raw Data file doesn´t contain enough points to make a plot.

59 A Software error occured. A Raw Data file cannot be opened after Display/ Plot, restart data collection. If the problem persists please send a Software Performance Report.

60 Error during data collection program. System parameter file cannot be opened by Data collection. Apparently the system parameter file has been corrupted while APD was active. Use the back-up disc or make a new copy of the master disc. Refer to Chapter 14.4.1.

63 Error during data collection program. A Raw Data file cannot be created, the reason can be:
- The disc is full : use Tidy up, or mount a new disc.
- The Index file of the disc is full : use Tidy up, or mount a new disc.
- The disc is Write Protected : switch off WRITE PROT on disc unit.
- The disc has not been mounted : mount the disc.

64 Error during data collection program. Error during opening of Work file, this should not occur, please send a Software Performance Report.

65 Error during data collection program. Error during opening of Log file, data collection continues after this warning. This could be one of the problems described in error 063.

70 A Software error occured. Boot the system (or give @LBO:[1,2]APDSTRTUP). If the problem persists please send a Software Performance Report.

71 A Software error occured. Boot the system (or give @LBO:[1,2]APDSTRTUP). If the problem persists please send a Software Performance Report.

80 Inconsistent job number in Batch file. Restart data collection. This problem should never occur, please send a Software Performance Report.

81 Inconsistent analysis program number in Batch file. Restart data collection. This problem should never occur, please send a Software Performance Report.

82 Inconsistent sample number in Batch file. Restart data collection. This problem should never occur, please send a Software Performance Report.

83 Inconsistent scan number in Batch file. Restart data collection. This problem should never occur, please send a Software Performance Report.

84 Inconsistent phase number in Batch file. Restart data collection. This problem should never occur, please send a Software Performance Report.

100 Licensee´s name corrupted.

103 System Parameter File does not exist. It has probably been deleted. Use the back-up disc, or make a new copy of the "master" disc. Refer to Chapter 14.4.1.

104 Cannot open System Parameter File. See the FCS code (15.4 in this chapter), and take the appropriate action.

105 Error in System Parameter File. Make a new copy of the "master" disc. Refer to Chapter 14.4.1.

106 This is a non-specified terminal; reassemble system parameters.

107 Error in System Parameter File; reassemble terminals part of system parameters.

111 No plot device available, plot program cannot be used.

140 Diffractometer system not specified, reassemble the diffractometer part of the system parameters.

141 Error in system parameters. See the FCS code (15.4 in this chapter), or make another copy of the "master" disc (refer to Chapter 14.4.1).

143 Diffractometer number should be between 1 and 4.

144 Unknown file name extension requested for printout.

145 Last specified terminal cannot be deleted.

146 Wrong terminal number, or this terminal has to be specified first.

147 Terminal number is operator´s terminal, it cannot be deleted.

148 This diffractometer is not specified, it cannot be deleted.

149 This diffractometer is not specified, it cannot be deleted.

150 Error in System Parameter File. Make a new copy of the "master" disc. Refer to Chapter 14.4.1.

151 This terminal number is already in use for a terminal.

152 This terminal number is already in use for a plotter.

153 File specifier format incorrect, it should be Dev:[g,m]name.type;vs.

154 The maximum allowable number of terminals have already been specified.

155 The maximum allowable number of diffractometers have already been specified.

160 The maximum number of lines in pattern of standard has been reached.

161 Error in Calibration File, see the FCS code (15.4 in this chapter), and take the appropriate action.

162 Error in Calibration File, see the FCS code (15.4 in this chapter), and take the appropriate action.

163 Error in Calibration File, see the FCS code (15.4 in this chapter), and take the appropriate action.

164 Error in DI File, see the FCS code (15.4 in this chapter), and take the appropriate action.

200 Error during start-up of diffractometer. The diffractometer number in this request for data collection has not been initialized in SETUPAPD.

201 File with this name is not on this disc with this UFD.

202 The necessary information is not in Batch File, assemble again.

203 This file does not contain batch file data, rename or reassemble.

204 No disc space available, tidy-up disc, copy and delete RD files.

205 Data collection impossible, re-initialize APD system software.

205 Data collection stopped, start data collection again.

207 Software error occurred. This problem should never occur, please send a Software Performance Report.

208 Software error occurred. This problem should never occur, please send a Software Performance Report.

999 *** Subroutine not YET available ***

15.3 FORTRAN ERRORS

There are 18 FORTRAN errors applicable to the APD1700 package, they are:

29 NO SUCH FILE. A file with the specified name could not be found during an OPEN operation.

30 OPEN FAILURE. FCS has detected an error during an OPEN operation. This message is used when the error condition is not one of the more common conditions for which specific error messages are issued. The file could be locked, or the disc could be almost full (refer to Chapter 14.4).

32 INVALID LOGICAL UNIT NUMBER. A logical unit number outside the range specified by the TKB UNITS= option, was used. This message will also be given if an attempt is made to close a file that is not open.

This problem should never occur, if it does please send a Software Performance Report.

34 UNIT ALREADY OPEN. A DEFINEFILE statement, CALL ASSIGN, or CALL FDBSET which specified a logical unit already opened for input/output was attempted.

This problem should never occur, if it does please send a Software Performance Report.

37 INCONSISTENT RECORD LENGTH. An existing direct access file, whose record length is not the same as specified in the DEFINEFILE statement, has been opened. Ensure that the file was created as a direct access file. The record length is not changed.

This problem should never occur, if it does please send a Software Performance Report.

38 ERROR DURING WRITE. FCS has detected an error while writing. Check the FCS code to get more information about the cause of the error.

39 ERROR DURING READ. FCS has detected an error while reading. Check the FCS code to get more information about the cause of the error.

41 NO FCS BUFFER ROOM. There is not enough free core left in the File Control Services buffer area to set up the required I/O buffers. Rebuild the task with a larger ACTFIL declaration, or reduce the level of multi-buffering.

This problem should never occur, if it does please send a Software Performance Report.

43 FILE NAME SPECIFICATION ERROR. The filename string used in a CALL ASSIGN is syntactically invalid, contains a switch specification, references to an undefined device mnemonic, or is in some other way not acceptable to the operating system. This error also occurs if you try to start the program from a non-existent UFD. You could have changed it with the SET DEFAULT command, or the disc with your UIC is not present.

63 OUTPUT CONVERSION ERROR. During a formatted output operation, the value of a particular number could not be output in the specified field length without loss of significant digits. The field is filled with asterisks (*), the program will not be interrupted.

70 INTEGER OVERFLOW. During an integer multiplication, division, or exponentiation operation, the value of the result exceeded 32767 in magnitude. Please send a Software Performance Report.

71 INTEGER ZERO DIVIDE. During an integer mode arithmetic operation an attempt was made to divide by zero. Please send a Software Performance Report.

72 FLOATING OVERFLOW. During an arithmetic operation a real value has exceeded the largest representable real number. The result of the operation is set to zero. Please send a Software Performance Report.

73 FLOATING ZERO DIVIDE. During a REAL mode arithmetic operation an attempt was made to divide by zero. The result of the operation is set to zero. Please send a Software Performance Report.

74 FLOATING UNDERFLOW. During an arithmetic operation a real value has become less than the smallest representable real number, and has been replaced with a value of zero. Please send a Software Performance Report.

83 LOGARITHM OF NEGATIVE VALUE. An attempt was made to take the logarithm of zero or a negative number. The result returned is zero. Please send a Software Performance Report.

84 SQUARE ROOT OF NEGATIVE NUMBER. An attempt was made to take the square root of zero or a negative number. The result returned is zero. Please send a Software Performance Report.

91 COMPUTER GOTO OUT OF RANGE. Control is passed to the next executable statement. Please send a Software Performance Report.

15.4 FILE CONTROL SERVICES (FCS)

Information about the File Control Services error will be displayed if you exit from APD and type "HELP FCS n", where "n" is the negative error number. The errors, together with their meaning, and if necessary rectification actions are given below:

-03 DEVICE NOT READY. Disc not inserted, wait until READY lamp is lit.

-04 PARITY ERROR ON DEVICE. Read error, call Field Service for the disc device.

-10 END OF FILE DETECTED.

-12 WRITE ATTEMPTED TO LOCKED UNIT. The disc is "write protected", take the required action.

-16 PRIVILEGE VIOLATION. An attempt was made to read from or write to a protected UFD to which access is not allowed.

-24 DEVICE FULL. The disc is full, tidy the disc up, or use another disc.

-25 INDEX FILE FULL. The index file table on the disc is full, this doesn't imply that the disc is full. The possible solutions are:
- Initialize another disc with a larger index file INI.
- Copy disc by using BRU.
- Tidy up the disc.
- Use another disc.

-26 NO SUCH FILE.

-27 LOCKED FROM READ/WRITE ACCESS. The disc is "Write protected", or the disc is software protected for read actions.

-29 ACCESSED FOR WRITE. Another program/user has already opened the file.

-30 FILE HEADER CHECKSUM FAILURE. Disc file corrupted.

-32 FILE PROCESSOR DEVICE READ ERROR. An error occured during read.

-33 FILE PROCESSOR DEVICE WRITE ERROR. An error occured during write.

-34 FILE ALREADY ACCESSED ON LUN.

-35 FILE ID, FILE NUMBER CHECK. Call Field Service for the disc device.

-36 FILE ID, SEQUENCE NUMBER CHECK. Call Field Service for the disc device.

-38 FILE WAS NOT PROPERLY CLOSED. The file is locked. Unlock the file by using either the UNLOCK command or PIP <name>/UN.

-39 OPEN - NO BUFFER SPACE AVAILABLE FOR FILE. Please send a Software Performance Report.

-48 RENAME - 2 DIFFERENT DEVICES.

-49 RENAME - NEW FILE NAME ALREADY IN USE.

-50 BAD DIRECTORY FILE. The directory cannot be read, it may be that a new disc has been inserted without dismount/mount commands.

-52 BAD DIRECTORY SYNTAX.

-56 BAD BLOCK ON DEVICE. Back-up the disc, run "BAD".

-66 BLOCK CHECK, CRC, OR FRAMING ERROR. During transfer of data, interruption of, or interference with the data occurred. Check connections (for example, the cable) and try again.

This Appendix will be issued later.

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